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(54) ORGANOPOLYSILOXANE COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain excellent shelf stability by employing an organopolysiloxane, an organohydrodienepolysiloxane, a compound having an active hydrogen atom-containing group, a first platinum group element catalyst, a second platinum group element catalyst, an addition reaction inhibitor and a filler.

SOLUTION: A composition comprises 100 pts.wt.

organopolysiloxane represented by formula I, 0.1-50 pts.wt.

organohydrodienepolysiloxane represented by formula II as a

crosslinking agent, 0-20 pts.wt. compound having an active

hydrogen atom-containing group, a thermoplastic resin having a melting point or a softening point of 40-200° C, 1-

1,000 ppm first platinum group element embedded in a

thermoplastic silicone resin or a heat melting compound

having a molecular weight of 1,000 or less, a second

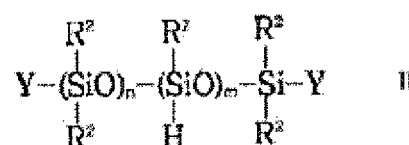
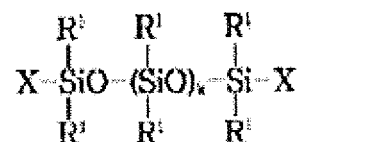
platinum group element in an amount of one tenth of the

first platinum group element, 0.001-20 pts.wt., addition

reaction inhibitor and 0-1,000 pts.wt. filler. In the formulas,

R¹ and X are each a 1-10C alkyl or aryl, a hydroxyl group or

the like; R² is a 1-10C alkyl or aryl, or the like; Y is H or a monovalent group; K is 4 or more, m is 1 or more; and n is 0 or more.



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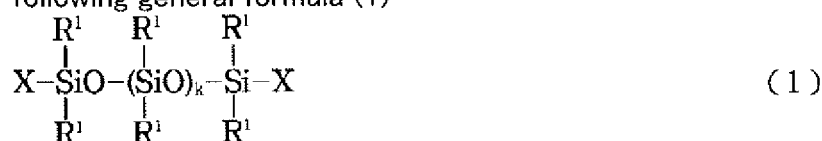
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CLAIMS

[Claim(s)]

[Claim 1](A) Organopolysiloxane 100 weight section, [Chemical formula 1] which are shown with a following general formula (1)



R¹ in formula and X -- an alkyl group of the carbon numbers 1-10, and an aryl group. [however,] an aralkyl group, an alkenyl group, a basis by which some hydrogen atoms combined with a carbon atom of these bases were replaced with a halogen atom and a basis chosen from a hydroxyl group, and k show four or more integers -- the inside of R¹ and the whole quantity of X -- an alkenyl group and/or a hydroxyl group -- 0.001-1-mol % -- it contains.

(B) ORGANO hydrogen polysiloxane 0.1 shown with a following general formula (2) which has in a molecule the hydrogen atom combined with at least three silicon atoms - 50 weight section,

[Chemical formula 2]



however, R² in formula -- an alkyl group of the carbon numbers 1-10, and an aryl group. As for an aralkyl group and a basis for which some hydrogen atoms combined with a carbon atom of these bases are chosen from a univalent basis replaced with a halogen atom, an atom which is chosen from a hydrogen atom and R² as for Y or a univalent basis, and m, zero or more integers and m+n of one or more integers and n are the integers of 3-500.

(C) Thermoplastic organic resin whose zero to compound 20 weight section which has an active hydrogen group, (D) melting point, or softening temperature is 40-200 **, Thermoplastic silicone resin and a platinum metal catalyst to which embedding of the molecular weight was carried out by either which is chosen from 1,000 or less heat colliquative compound As a platinum metal atom, to the whole quantity of a constituent 1-1,000 ppm, (E) Quantity which supplies a platinum metal atom of quantity of 1/10 or less weight of a platinum metal atom supplied from a platinum metal catalyst (D) ingredient, (F) An organopolysiloxane constituent which contains 0.001 to addition reaction depressant 20 weight section, and (G) bulking agent 0 - 1,000 weight section, and is characterized by things.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the organopolysiloxane constituent excellent in preservability and hardenability.

[0002]

[Description of the Prior Art]From before, the addition reaction by the platinum metal catalyst of an aliphatic unsaturated group and a hydrosilyl group is used for many fields, and especially a platinum compound, It is used as a catalyst compound with the highest flexibility in these fields, and is used for organic synthesis reactions, such as composition of a sill alkane bond, and also especially in the field of silicone industry, It is used as a means of bridge construction of addition reaction type resin or rubber, and is used for the use of extrusion by adhesives, a coating agent, a potting agent, gel, foam, and liquefied or millable rubber, compression molding, or injection molding as a concrete use.

[0003]In recent years, in the field of silicone industry, the material which a retention period hardens for a long time and promptly from a viewpoint of processability and workability is called for, and many are proposed about the constituent which used the addition reaction by platinum metal catalyst use as a bridge construction system for this reason. Many technology about the controlling agent for controlling the shelf life of a platinum metal catalyst and pot life in connection with this is also indicated, For example, a benzotriazol system compound (JP,S40-25069,B), An acetylene alcohol system compound (JP,S44-31476,B), A vinyl group content polysiloxane compound (JP,S48-10947,B), hydroperoxide (JP,S57-20340,B), an amine compound (JP,S63-56563,A), etc. are proposed.

[0004] The method by such chemical control has a limit in the balance of working life and a cure rate, and it is becoming impossible however, to be unable to cope with the market demand currently asked for still longer preservability and sharp hardenability.

[0005]Then, embedding of the platinum metal catalyst is carried out to thermoplastics, silicone resin, etc. which have the specific melting point, it is encapsulated, it blends into a constituent, and the method of making a platinum metal catalyst emit into a silicone composition by the dissolution by melting of these resin by heating or a solvent is proposed. As a prior art reference about this technology, for example JP,S49-134786,A, There are JP,S58-37053,A, JP,S64-51140,A, JP,H2-9448,A, JP,H2-14244,A, JP,H5-202193,A, JP,H7-196921,A, etc.

[0006]However, since a high-concentration platinum metal catalyst is unevenly distributed and exists in a constituent, the method by this microencapsulation has the problem of being easy to cause partial hardening.

[0007]Then, in order to solve the problem of this point, the methods (JP,H4-46962,A etc.) of using acetylene alcohol etc. as an reaction inhibitor are proposed, and preventing a partial hardening reaction is indicated.

[0008]However, when this constituent was also developed for various uses, it became clear that

some faults arose.

[0009] For example, when adding adhesion components to these constituents and using as heat cure type silicone rubber adhesives, The temperature setting in a mass-production line is comparatively low, and if fixed time is taken for the thermoplastics etc. which are carrying out embedding of the platinum metal catalyst to dissolve, the problem to which hardening and adhesion in a factory line become imperfect will sometimes arise. When blending hydroxyl supply sources, such as alcohol or water, with a constituent and obtaining foam in a heating line, it is known that foaming by a little dehydrogenation in early stages of a reaction will serve as the core, and good foam will be obtained, but. The above-mentioned reaction inhibitor also controls this initial foaming, and there is a problem of being unable to obtain good foam. When using it as an addition hardening material of a millable type and it vulcanizes at high speed in order to mold an electric wire, a tube, etc., a tuck (feeling of adhesion) remains in the surface, and there are problems -- the molding body which has the smooth surface is not obtained.

[0010] Therefore, an object of this invention is to provide the organopolysiloxane constituent which solved the above-mentioned problem.

[0011]

[The means for solving a technical problem and an embodiment of the invention] As opposed to the organopolysiloxane constituent which contains organopolysiloxane containing an alkenyl group or a hydroxyl group, and the ORGANO hydrogen polysiloxane as a result of inquiring wholeheartedly, in order that this invention person may attain the above-mentioned purpose, (D) Thermoplastic organic resin, thermoplastic silicone resin whose melting point or softening temperature is 40-200 **, A molecular weight to the whole quantity of a constituent as a platinum metal catalyst platinum metal atom by which embedding was carried out by either which is chosen from 1,000 or less heat colliquative compound And 1-1,000 ppm, (E) Use together in the quantity which supplies the platinum metal atom of the quantity of 1/10 or less weight of the platinum metal atom supplied from the platinum metal catalyst (D) ingredient by which embedding is not carried out with thermoplastics etc., and. By blending an addition reaction depressant, excel in preservability, and working life is long, and. The problem which hardenability was good, hardened promptly at the time of heat cure, and moreover mentioned above, namely, the case where it takes time when the temperature setting in a mass-production line is comparatively low, and it is fixed although the thermoplastics etc. which carry out embedding of the platinum metal catalyst dissolve when adhesion components are added and it uses as heat cure type silicone rubber adhesives -- the problem that hardening and adhesion are imperfect in these factory lines. When hydroxyl supply sources, such as alcohol or water, are used together to the above-mentioned constituent and foam is too made profitably like in a heating line as foam, The difficulty of initial foaming not being controlled, either and being unable to obtain good foam, When molding an electric wire and a tube in the addition hardening material of a millable type, and vulcanization at a high speed was performed, the tuck (feeling of adhesion) remained in the surface, and the knowledge of the ability to solve difficulties -- the smooth surface cannot be obtained -- was carried out.

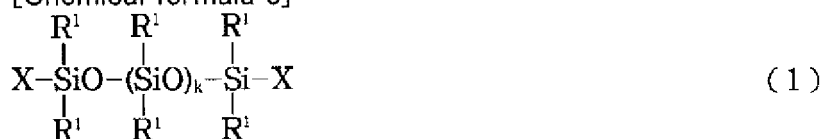
[0012] Namely, according to this invention, protect with thermoplastics etc. 90weight % or more of the platinum metal catalyst of the quantity which an addition reaction completes by within a time [fixed] on a design (as a platinum metal atomic weight), and control the change at the time of preservation, and. Coexistence with preservability and hardenability can be aimed at by considering it as the reaction control system by the chemistry coordination conventionally used in the state where embedding of 10 or less weight % of a platinum metal catalyst is not carried out with thermoplastics etc. (as a platinum metal atomic weight).

[0013] Therefore, organopolysiloxane 100 weight section this invention is indicated to be with the (A) following general formula (1), (B) ORGANO hydrogen polysiloxane 0.1 shown with the following general formula (2) which has in a molecule the hydrogen atom combined with at least three silicon atoms - 50 weight section, (C) Thermoplastic organic resin whose zero to compound 20 weight

section which has an active hydrogen group, (D) melting point, or softening temperature is 40–200 **, Thermoplastic silicone resin and platinum metal catalyst to which embedding of the molecular weight was carried out by either which is chosen from 1,000 or less heat colligative compound As a platinum metal atom, to the whole quantity of a constituent 1–1,000 ppm, (E) The quantity which supplies the platinum metal atom of the quantity of 1/10 or less weight of the platinum metal atom supplied from a platinum metal catalyst (D) ingredient, (F) Contain 0.001 to addition reaction depressant 20 weight section, and (G) bulking agent 0 – 1,000 weight section, and provide the organopolysiloxane constituent characterized by things.

[0014]

[Chemical formula 3]



R¹ in formula and X -- the alkyl group of the carbon numbers 1–10, and an aryl group. [however,] an aralkyl group, an alkenyl group, the basis by which some hydrogen atoms combined with the carbon atom of these bases were replaced with the halogen atom and the basis chosen from a hydroxyl group, and k show four or more integers -- the inside of R¹ and the whole quantity of X -- an alkenyl group and/or a hydroxyl group -- 0.001–1–mol % -- it contains.

[0015]

[Chemical formula 4]



however, R² in formula -- the alkyl group of the carbon numbers 1–10, and an aryl group. As for an aralkyl group and the basis for which some hydrogen atoms combined with the carbon atom of these bases are chosen from the univalent basis replaced with the halogen atom, the atom which is chosen from a hydrogen atom and R² as for Y or a univalent basis, and m, zero or more integers and m+n of one or more integers and n are the integers of 3–500.

[0016] If lessons is taken from this invention and it explains in more detail hereafter, as mentioned above, organopolysiloxane will be used for the organopolysiloxane constituent of this invention as a (A) ingredient. This (A) ingredient is base polymer of this constituent, is organopolysiloxane of straight chain shape fundamentally, and is shown by the following general formula (1).

[0017]

[Chemical formula 5]



[0018] Here, the above-mentioned R¹ and X are the carbon numbers 1–10, the alkyl group of 1–8, an aryl group, an aralkyl group, an alkenyl group and the basis by which some hydrogen atoms on the carbon atom of these bases were replaced with the halogen atom, and a basis chosen from a hydroxyl group preferably. Specifically A methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, An isobutyl group, a tert-butyl group, a pentyl group, a hexyl group, a cyclohexyl group, Alkyl groups, such as an octyl group, a nonyl group, and a decyl group, a vinyl group, an allyl group, Alkenyl groups, such as a propenyl group, an isopropenyl group, a butenyl

group, and a hexenyl group, Although halogenated hydrocarbon groups, such as aralkyl groups, such as aryl groups, such as a phenyl group and a tolyl group, benzyl, and a phenylethyl group, a chloromethyl group, a bromoethyl group, and a 3,3,3-trifluoropropyl group, and a hydroxyl group can be illustrated, it is not limited to these. In this case, although R^1 and X may be mutually the same or it may differ, it is [R^1 and 0.001–1 mol% of the whole quantity of X] especially required for 0.02–0.8–mol % to be an alkenyl group and/or a hydroxyl group. If they are a functional group which contributes to crosslinking reaction, their intensity of a hardened material is weak when an alkenyl group and a hydroxyl group have less the quantity than 0.001–mol %, and they become a thing without intensity, and do not function as a rubber elastomer and there are than 1–mol %, they will become what has a hardened material high crosslinking density and weak. [more] As for a hydroxyl group, it is preferred to have combined only with the silicon atom of chain both ends as a functional group which contributes to crosslinking reaction, and an alkenyl group, Even if it has combined with which silicon atom in the middle of chain both ends or a chain, it has combined with both, but it is preferred that it is what contains the alkenyl group combined with the silicon atom of chain both ends at least in respect of the physical properties of a hardened material, etc. As for X, it is [a vinyl group or a hydroxyl group, and R^1] preferred from points, such as the ease of carrying out of acquisition, and cost, to be chosen from a methyl group, a phenyl group, a 3,3,3-trifluoropropyl group, and a vinyl group.

[0019] A hardened material becomes it weak preferably that it is 100 or more integers and k is three or less still more preferably 50 or more four or more, and k cannot be used as a molding body. in addition -- although a maximum in particular of k is not restricted -- usually -- 15,000 -- it may be about 8,000 preferably, and organopolysiloxane of this invention may be the shape of liquid, and paste state, or may be crude rubber-like.

[0020] The (B) ingredient of this invention is the ORGANO hydrogen polysiloxane shown with a following general formula (2), and acts as a cross linking agent or a cross linking agent and foaming agent.

[0021]

[Chemical formula 6]



[0022] here -- the above-mentioned R^2 -- the carbon numbers 1–10 -- desirable -- an alkyl group of 1–8. Some hydrogen atoms on a carbon atom of an aryl group, aralkyl groups, and these bases are the bases chosen from a univalent basis replaced with a halogen atom, and Y is an atom or a univalent basis chosen from a hydrogen atom and R^2 . Although the same thing as what was illustrated in R^1 as an alkyl group, an aryl group, an aralkyl group, and a halogenated hydrocarbon group here in R^2 or Y can be illustrated, It is preferred that it is what does not contain an aliphatic unsaturated group as this R^2 or Y, and this ORGANO hydrogen polysiloxane needs in a molecule to have the hydrogen atom (namely, SiH group) combined with at least three silicon atoms. n -- zero or more -- desirable -- 0–499 -- an integer of 0–199 is shown still more preferably -- m -- one or more -- desirable -- 3–500 -- an integer of 4–200 is shown still more preferably -- a value of n+m -- 3–500 -- it is an integer of 4–200 preferably.

[0023]. The above-mentioned (B) ingredient is a cross linking agent reacted to the above-mentioned (A) ingredient. [(that is, an alkenyl group in the (A) ingredient and a SiH group in the (B) ingredient add by hydrosilylation, or a silanol group in the (A) ingredient and a SiH group in the (B) ingredient add by dehydrogenation), and] The (C) ingredient and dehydrogenation of an optional component

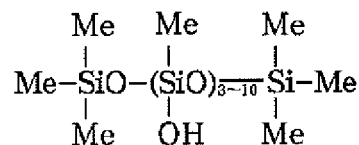
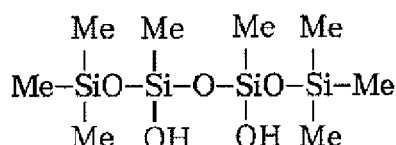
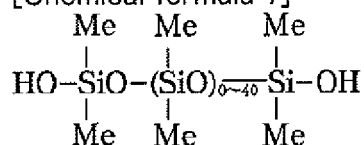
which are mentioned later are caused, it acts also as a foaming agent, and especially the loadings need to carry out 1–25 weight–section combination 0.1 to 50 weight section to base polymer 100 weight section of the (A) ingredient. When there are few loadings than 0.1 weight sections, bridge construction fully becomes impossible, and if more than 50 weight sections, or bridge construction becomes impossible too. [weatherability]

[0024] A hydroxyl group (namely, silanol group) which the (A) ingredient combined with a silicon atom is not contained, And in not blending the (C) ingredient mentioned later (it is not necessary to make a constituent foam and to make form or sponge form). (A) To 1 mol of alkenyl groups in an ingredient, the (B) ingredient can also be blended so that a mole ratio of a SiH group in the (B) ingredient may become 0.5–10, especially one to about 5.

[0025] Next, it is a compound which has active hydrogen, when a constituent of this invention is used for the (C) ingredient of this invention as a constituent for foam, it is a required ingredient, but if it is not necessary to make a constituent foam and to make form or sponge form, it can omit the combination. Here, a compound which has active hydrogen means a compound which has a hydrogen atom (for example, hydroxy group) which can carry out dehydration to a SiH group in the (B) ingredient in response to the bottom of existence of a platinum metal catalyst in [at least one] a molecule. Although a publicly known compound can be used as a compound which has active hydrogen, don't deactivate the catalytic activity of a platinum metal catalyst which is (D) and the (E) ingredient which are mentioned later. the carbon numbers 1–20 which specifically have one piece or two OH radicals or more in water and one molecule -- desirable -- about one to 12 alcohol compound. Silang containing a silanol group or 2–50 silicon atoms -- compounds, such as about two to 20 siloxane, preferably, [mention and] What is shown in methanol, ethanol, n-propanol, iso-propanol, butanol, ethylene glycol, a diethylene glycol, glycerin, a trimethyl silanol, diphenylsilanediol, and a following formula is illustrated. These can mix independent or two sorts or more, and can use one sort.

[0026]

[Chemical formula 7]



(Me shows a methyl group.)

[0027] The loadings of the above-mentioned (C) ingredient carry out 0.1–15 weight–section combination 0.1 to 20 weight section, especially when using it as 0 – 20 weight section, especially a constituent for foam to base polymer 100 weight section of the above-mentioned (A) ingredient.

[0028] The (D) ingredient of this invention is the platinum metal catalyst which it *****ed. In this invention, a platinum metal catalyst means platinum metal atoms, such as platinum, palladium, and rhodium, the simple substance of a platinum metal which contains a

platinum atom preferably, platinum metal compounds, and those complexes as catalyst metal. [0029] Although the (D) ingredient of this invention acts as a catalyst for carrying out the addition reaction of the above-mentioned (A) ingredient and the (B) ingredient, In order to raise the preservability of a constituent, it is considered as the platinum metal (that is, it *****ed) catalyst by which embedding was carried out with either [which has the melting point of 40-200 ** or softening temperature] thermoplastic organic resin, thermoplastic silicone resin and a with a molecular weight of 1,000 or less heat colliquative compound. This (D) ingredient can show the activity of a platinum metal catalyst above near the melting point (or softening temperature) of the compound which carries out embedding, and can be contributed to hardening and/or foaming of a constituent. Therefore, although the melting point or softening temperature of the above-mentioned thermoplastic organic resin, thermoplastic silicone resin, and a with a molecular weight of 1,000 or less heat colliquative compound is chosen by the use and preservation conditions which use the constituent of this invention, especially in this invention, it requires that it is 50-150 ** at 40-200 **. The preservability in ordinary temperature is not enough in it being less than 40 **, and if it exceeds 200 **, preservability is enough, but the difficulty that hardening takes time arises.

[0030] As thermoplastic organic resin, in this case, polyolefin resin, polystyrene resin, Organic resin other than silicone series, such as an acrylic resin and cellulose type resin, is mentioned, As thermoplastic silicone resin (namely, organopolysiloxane resin of the three-dimensional network structure containing branching structures, such as 3 functionality siloxane units and/or a SiO₂ unit), although selection use of the various things is carried out, The silicone resin which has aliphatic unsaturated groups, such as a phenyl group or a perfluoroalkyl group (for example, 3,3,3-trifluoropropyl group), and an alkenyl group (for example, a vinyl group, an allyl group, a propenyl group), is preferred. A molecular weight 1,000 or less heat colliquative compound, Are heat colliquative compounds other than the above-mentioned thermoplastic organic resin and thermoplastic silicone resin, and as this heat colliquative compound, 2-butene 1,4-diol, diphenylacetylene, 4-hexyl resorcinol, 2-vinylnaphthalene, 2-acetyl-1-tetralone, the 2, 5-diphenyloxazole, 3,6-dichloro pyridazine, 2,5-torr quinone, 3,6-dimethyl- 4-octyne-3,6-diol, Bis(2, 2, 6, and 6-tetramethyl 4-piperidinyl)SEBUKETO, 3,3'-thiodipropionic acid-di-n-octadecyl, 2,4,7,9-tetra-methyl-5-decyne-4,7-diol, 2,5-dimethyl-3-hexyne-2,5-diol, 1,3-bis(trimethylsilyl ethynyl) benzene, a thiocumarone 4-ol, etc. are usable.

[0031] On the other hand as a platinum metal catalyst by which embedding is carried out to the above-mentioned resin or a heat colliquative compound, They are platinum metals, such as platinum, rhodium, and palladium, and a catalyst which contains platinum preferably especially, Various complexes etc. which are derived from platinum black more publicly known than before as an addition reaction catalyst, chloroplatinic acid, or this are mentioned, Specifically, a complex of a denaturing alcohol thing of platinum black, chloroplatinic acid, and chloroplatinic acid, chloroplatinic acid, an olefin, aldehyde, a vinyl siloxane, acetylene, and acetylene alcohol, etc. can be mentioned.

[0032] As such a (D) ingredient, JP,S49-134786,A, As for silicone resin which can mention a platinum metal catalyst etc. by which embedding was carried out, and is used here by silicone resin which is indicated to JP,H4-46962,A etc., it is preferred that it is a thing having a phenyl group or a perfluoroalkyl group, and an aliphatic unsaturated group. a platinum metal catalyst by which embedding was carried out with thermoplastic organic resin currently indicated by JP,S64-47442,A, such as polystyrene and polyolefine, as other examples — further, A molecular weight which does not belong under the category of the above-mentioned thermoplastic organic resin can mention a platinum group compound etc. by which embedding was carried out with 1,000 or less heat colliquative compound.

[0033] As a manufacturing method of the platinum metal catalyst by which embedding was especially carried out with the heat colliquative compound, Although publicly known methods, such as a method indicated in the gazette etc. which were mentioned above, may be used and it is not

restricted in particular, it can obtain by contacting a heat colliquative compound and a platinum group compound in fusion or the solution state of a heat colliquative compound, for example. The solid catalyst which the platinum metal catalyst distributed uniformly is acquired by heating here more than the melting point of a compound, when performing a thermal melting solution, making a platinum metal catalyst support with the state where it was made to equalize or distribute in a solvent, when dissolving, cooling or solvent distilling off and solidifying this. In addition, [whether misty state is made to spray and solidify these by the liquid state in fusion or the dissolution, and] Or perform solvent removal and it is made to emulsify with an emulsifier by the method by the spray dry which obtains particles, and underwater, and it cools below to the solidification temperature of a solvent, dissolving in the method and solvent which acquire a solid catalyst, and the method of acquiring a solid catalyst with what is called a freeze drying method etc. that perform solvent removal under decompression, etc. are mentioned. Thus, it may use as a granular material, and it can be again made a slurry or paste state, can be made to be able to distribute by silicone oil, and the acquired solid catalyst can also be used.

[0034]The loadings of the above-mentioned (D) ingredient are the quantity supplied 1-1,000 ppm as a platinum metal atom to the constituent whole quantity, and a quantity preferably set to 5-200 ppm.

[0035]The (E) ingredient of this invention is a platinum metal catalyst, and this uses platinum metal catalyst itself by which shows the meaning mentioned above and embedding is not carried out to thermoplastic organic resin, thermoplastic silicone resin, and a heat colliquative compound. This complements the function as an addition reaction catalyst of the above-mentioned (D) ingredient, specifically makes an initial set and initial foaming good, and when it fabricates an electric wire, a tube, etc. with which especially high-speed vulcanization is performed, it can cancel the surface tackiness (feeling of adhesion) etc. which pose a problem.

[0036]A publicly known platinum metal catalyst can be conventionally used for the above-mentioned (E) ingredient, and, unlike the above-mentioned (D) ingredient, a platinum metal catalyst, Without carrying out embedding with thermoplastics, thermoplastic silicone resin, and a heat colliquative compound, as mentioned above as it is, It is blended into a constituent and the complex of the denaturing alcohol thing of platinum black, chloroplatinic acid, and chloroplatinic acid, chloroplatinic acid, an olefin, aldehyde, a vinyl siloxane, acetylene, and acetylene alcohol, etc. can specifically be illustrated.

[0037]The quantity of the platinum metal atom in the (E) ingredient the loadings of the above-mentioned (E) ingredient by a weight ratio to the quantity of the platinum metal atom supplied from the above-mentioned (D) ingredient 1/10 or less. 1/20 or less is used preferably -- the weight ratio of the above [the minimum] -- 1/100,000 (0.001%) -- desirable -- 1/1,000 (0.1%) -- it is especially 1/100 (1%). When there are too many additions, it becomes impossible to hold the balance of preservability and hardenability. When there are too few additions, the effect by concomitant use of the (D) ingredient and the (E) ingredient may not be acquired.

[0038]Although the addition reaction depressant which is the (F) ingredient of this invention can be used in order to control the reaction by the platinum metal atom supplied from the above-mentioned (E) ingredient, and a thing more publicly known than before can be used, Specifically A benzotriazol system compound (JP,S40-25069,B), An acetylene alcohol system compound (JP,S44-31476,B), A vinyl group content polysiloxane compound (JP,S48-10947,B), It can choose from hydroperoxide (JP,S57-20340,B), an amine compound (JP,S63-56563,A), etc., and can choose from acetylene or an acetylene alcohol content compound suitably. 3-methyl-1-butyn-3-ol, 3-methyl-1-pentyn-3-ol, ethynylcyclohexanol, 3,5-dimethyl-1-hexyn-3-ol, etc. can more specifically be mentioned.

[0039]Although the loadings of the above-mentioned (F) ingredient change with the structure of the (F) ingredient, and molecular weights, In this invention, to above-mentioned (A) ingredient 100 weight section, 0.001 - 20 weight section, It is preferred that it is the quantity which turns into 2-500 Eq especially about 1-1,000 Eq to the platinum metal atom which is preferably made into the

range of 0.002 to 5 weight section, and is fundamentally supplied as a (E) ingredient.

[0040]The bulking agents which are the (G) ingredients of this invention are the arbitrary ingredients added for increase in quantity of a constituent or reinforcement of physical intensity and also flameproofing, thermal conductivity, and electrical conductivity, Specifically Haze-like pyrogenic silica, sedimentation nature silica, crystalline grinding silica, colloidal calcium carbonate, What processed precipitated calcium carbonate, heavy calcium carbonate, acetylene black, furnace carbon, titanium oxide, metal, a metallic oxide, and its surface with the silane compound and the siloxane compound is mentioned. To (A) ingredient 100 weight section, zero to 1,000 weight section, one to 1,000 weight section, the loadings of the (G) ingredient are 1 – 400 weight section, and if 1,000 weight sections are exceeded, combination is difficult, or its hardened material is weak and they become what was remarkably inferior in the mechanical property especially preferably.

[0041]Although the constituent of this invention can blend (A) – (G) ingredient mentioned above, The thixotropic improver which can also blend a publicly known additive agent if needed, and is specifically used in this industry as these additive agents, The silicone oil as an adhesive improver and a plasticizer, $R_3SiO_{1/2}$ unit for intensity reinforcement, and a SiO_2 unit are made into basic structure. Silicone resin including the structure where silicone resin or essential structure to contain are $RSiO_{3/2}$ unit can be added unless the purpose of this invention is checked (each R here.).

Monovalent hydrocarbon radicals, such as an alkyl group of the carbon numbers 1–8, an alkenyl group, and an aryl group, are shown.

[0042]In this case, as an adhesive improver, the carbon functional silane or siloxane which has a reactant group is effective, For example, gamma-glycidoxypopyltrimetoxysilane, gamma-acryloxypropyltrimethoxysilane, Epoxy functional groups, such as gamma-methacryloxypropyl trimethoxy silane, The alkoxysilane which has reactant groups, such as an acrylic functional group (bird), and its partial hydrolysis condensate, Methyl hydrogen polysiloxane of an end bird alkoxy-silyl-groups blockade, Can use trimethoxysilylpropyl denaturation annular methyl hydrogen polysiloxane, triallyl isocyanurate, etc., and the loadings, (A) They are about 0.01–10 weight sections more preferably 0.01 to 50 weight section zero to 50 weight section to ingredient 100 weight section.

[0043]Although the curing conditions of this invention constituent can be suitably selected in a use, it is usually carried out in the range for about 2 to 120 minutes at 60–150 **.

[0044]

[Effect of the Invention]Preservability and hardenability are [organopolysiloxane constituent of this invention] compatible.

[0045]

[Working example]Although the synthetic example of a catalyst, an working example, and a comparative example are given and this invention is explained concretely hereafter, this invention is not limited to the following working example. The part in the following example shows a weight section.

[0046][Example 1 of catalyst composition] As a platinum atom, in the 5,000 ppm toluene solution of a siloxane denaturation platinum complex, Tales doses of the phenyl groups and vinyl group content silicone resin containing $C_6H_5SiO_{3/2}$ unit with a melting point of 78 **, and $(CH_2=CH)SiO_{3/2}$ unit to toluene are added, It agitated until it became uniform, and the resin powder platinum catalyst (the catalyst 1, a platinum atomic weight: 5,000 ppm) was prepared by the spray-drying method.

[0047][Example 2 of catalyst composition] to 5 g of 3,6-dimethyl- 4-octyne-3,6-diol (melting point of 54 **). The vinyl group content siloxane complex 5g derived from chloroplatinic acid was added, and it heat-treated at 80 ** for 1 hour, and after carrying out a strip, it cooled and the solid hydrosilylation catalyst (the catalyst 2, a platinum atomic weight: 5,000 ppm) was prepared.

[0048][Example 3 of catalyst composition] with 5 g of 1,3-bis(trimethylsilyl ethynyl)benzene (melting point of 58 **). The vinyl group content siloxane complex 5g derived from chloroplatinic acid is added, It heat-treated at 80 ** for 1 hour, and after adding the polyglycerin system surface-active

agent 0.5g to this and carrying out emulsification to it underwater, it filtered and dried and the hydrosilylation catalyst (the catalyst 3, a platinum atomic weight: 5,000 ppm) of fine powder form was prepared.

[0049][Working example 1] The viscosity of 25 ** by which chain both ends were blocked with the vinyl dimethylsilyl group 100 copies of dimethylpolysiloxane of 30,000cp, It mixed until the surface put ten copies of haze-like silica of specific surface area [of 130 m] ²/g processed by dichlorosilane into the omnipotent mixer and became uniform, and the base compound was prepared.

[0050]The catalyst 1 acquired in the above-mentioned example 1 of catalyst composition to 100 copies of this base compound 2.0 copies (it is 100 ppm by platinum conversion to said base compound), The toluene solution of the same siloxane denaturation platinum complex as what was used in the example 1 of catalyst composition 0.1 copy (it is 5.0 ppm by platinum conversion to said base compound), And after agitating until it adds 0.002 copy of 2-ethylhexanol and becomes uniform with an omnipotent mixer, Both ends added 16 copies of methyl hydrogen polysiloxane which has the 0.005 mol/g SiH group blocked with the trimethylsilyl group, and were mixed, and the constituent 1 (the weight ratio of the platinum atom in the (E) ingredient to the platinum atom in the (D) ingredient is 0.05%) was obtained.

[0051][Working example 2] The viscosity of 25 ** by which chain both ends were blocked with the vinyl dimethylsilyl group 100 copies of dimethylpolysiloxane of 30,000cp, It mixed until the surface put ten copies of haze-like silica of specific surface area [of 130 m] ²/g processed by dichlorosilane into the omnipotent mixer and became uniform, and the base compound was prepared.

[0052]For water 0.2 copy and the catalyst 1 to 100 copies of this base compound 1.0 copy (it is 50 ppm by platinum conversion to a base compound), The toluene solution of the same siloxane denaturation platinum complex as what was used in the example 1 of catalyst composition 0.01 copy (it is 0.5 ppm by platinum conversion to a base compound), And after agitating until it adds 0.002 copy of 2-ethylhexanol and becomes uniform with an omnipotent mixer, The viscosity of 25 ** by which both ends were blocked with the trimethylsilyl group adds five copies and 0.3 copy of phenylsilane, and mixes methyl hydrogen polysiloxane (the amount of SiH groups is 0.016 mol/g) of 40cp, The constituent 2 (the weight ratio of the platinum atom in the (E) ingredient to the platinum atom in the (D) ingredient is 0.01%) was obtained.

[0053][Working example 3] The viscosity of 25 ** by which chain both ends were blocked with the vinyl dimethylsilyl group 100 copies of dimethylpolysiloxane of 30,000cp, It agitated until the surface put ten copies of haze-like silica of specific surface area [of 130 m] ²/g processed by dichlorosilane into the omnipotent mixer and became uniform, and the base compound was prepared.

[0054]For water 0.2 copy and the catalyst 2 to 100 copies of this base compound 1.0 copy (it is 50 ppm by platinum conversion to a base compound), The toluene solution of the same siloxane denaturation platinum complex as what was used in the example 1 of catalyst composition 0.01 copy (it is 0.5 ppm by platinum conversion to a base compound), And after agitating until it adds 0.002 copy of 2-ethylhexanol and becomes uniform with an omnipotent mixer, The viscosity of 25 ** by which both ends were blocked with the trimethylsilyl group adds five copies and 0.3 copy of phenylsilane, and mixes methyl hydrogen polysiloxane (the amount of SiH groups is 0.016 mol/g) of 40cp, The constituent 3 (the weight ratio of the platinum atom in the (E) ingredient to the platinum atom in the (D) ingredient is 0.01%) was obtained.

[0055][Comparative example 1] The viscosity of 25 ** by which chain both ends were blocked with the vinyl dimethylsilyl group 100 copies of dimethylpolysiloxane of 30,000cp, It agitated until the surface put ten copies of haze-like silica of specific surface area [of 130 m] ²/g processed by dichlorosilane into the omnipotent mixer and became uniform, and the base compound was prepared.

[0056]2.1-copy (it is 105 ppm by platinum conversion to base compound) addition of the catalyst 1 is carried out to 100 copies of this base compound, After agitating until it became uniform with the omnipotent mixer, both ends added 16 copies of methyl hydrogen polysiloxane which has SiH-group 0.005 mol/g blocked with the trimethylsilyl group, and were mixed, and the constituent 4 was obtained.

[0057][Comparative example 2] The viscosity of 25 ** by which chain both ends were blocked with the vinyl dimethylsilyl group 100 copies of dimethylpolysiloxane of 30,000cp, It agitated until the surface put ten copies of haze-like silica of specific surface area [of 130 m] ²/g processed by dichlorosilane into the omnipotent mixer and became uniform, and the base compound was prepared.

[0058]The toluene solution of the same siloxane denaturation platinum complex as what was used in the example 1 of catalyst composition to 100 copies of this base compound 2.1 copies (it is 105 ppm by platinum conversion to a base compound), And after agitating until it added 0.002 copy of 2-ethylhexanol and became uniform with the omnipotent mixer, both ends added 16 copies of methyl hydrogen polysiloxane which has SiH-group 0.005 mol/g blocked with the trimethylsilyl group, and were mixed, and the constituent 5 was obtained.

[0059]The [comparative example 3] Viscosity of 25 ** by which chain both ends were blocked with a vinyl dimethylsilyl group 100 copies of dimethylpolysiloxane of 30,000cp, It agitated until the surface put ten copies of haze-like silica of specific surface area [of 130 m] ²/g processed by dichlorosilane into an omnipotent mixer and became uniform, and a base compound was prepared.

[0060]The catalyst 1 to 100 copies of this base compound 2.1 copies (it is 105 ppm by platinum conversion to a base compound), And after agitating until it added 0.002 copy of 2-ethylhexanol and became uniform with an omnipotent mixer, both ends added 16 copies of methyl hydrogen polysiloxane which has SiH-group 0.005 mol/g blocked with a trimethylsilyl group, and were mixed, and the constituent 6 was obtained.

[0061]The [comparative example 4] Viscosity of 25 ** by which chain both ends were blocked with a vinyl dimethylsilyl group 100 copies of dimethylpolysiloxane of 30,000cp, It agitated until the surface put ten copies of haze-like silica of specific surface area [of 130 m] ²/g processed by dichlorosilane into an omnipotent mixer and became uniform, and a base compound was prepared.

[0062]For water 0.2 copy and the catalyst 2 to 100 copies of this base compound 1.01 copies (it is 50.5 ppm by platinum conversion to a base compound), And after agitating until it adds 0.002 copy of 2-ethylhexanol and becomes uniform with an omnipotent mixer, Viscosity of 25 ** by which both ends were blocked with a trimethylsilyl group added five copies and 0.3 copy of phenylsilane, and mixed methyl hydrogen polysiloxane (the amount of SiH groups is 0.016 mol/g) of 40cp, and the constituent 7 was obtained.

[0063][Working example 4] The viscosity of 25 ** by which chain both ends were blocked with the hydroxyl group 100 copies of dimethylpolysiloxane of 20,000cp, It agitated until the surface put ten copies of haze-like silica of specific surface area [of 130 m] ²/g processed by dichlorosilane into the omnipotent mixer and became uniform, and the base compound was prepared.

[0064]For water 0.2 copy and the catalyst 3 to 100 copies of this base compound 1.0 copy (it is 50 ppm by platinum conversion to a base compound), The toluene solution of the same siloxane denaturation platinum complex as what was used in the example 1 of catalyst composition 0.01 copy (it is 0.5 ppm by platinum conversion to a base compound), And after agitating until it adds 0.002 copy of 2-ethylhexanol and becomes uniform with an omnipotent mixer, The viscosity of 25 ** by which both ends were blocked with the trimethylsilyl group added five copies of methyl hydrogen polysiloxane (the amount of SiH groups is 0.016 mol/g) of 40cp, and was mixed, and the constituent 8 (the weight ratio of the platinum atom in the (E) ingredient to the platinum atom in the (D) ingredient is 0.01%) was obtained.

[0065] The following experiments were conducted on the obtained constituents 1-8. First, about the working example 1 and the comparative examples 1, 2, and 3, the difference of hardenability was checked with the curelast meter. The result of measurement is shown in Table 1.

[0066]

[Table 1]

		10 %トルク時間 (min)	90 %トルク時間 (min)	90 %トルク時間－ 10 %トルク時間 (min)
実施例	1	5.0	6.5	1.5
比較例	1	4.2	7.5	3.3
	2	0.8	1.6	0.8
	3	6.0	10.5	4.5

[0067] As shown in Table 1, in the usual microencapsulation platinum catalyst (namely, only (D) ingredient) of the comparative example 1, the time to the end of hardening from the standup of hardening has taken 3 minutes or more. In the system which added a little controlling agents to the platinum catalyst (namely, (E) ingredient) which is not processed [of the comparative example 2], sufficient working life in the part with short time to the standup of hardening and the room temperature was not obtained, but when saved at a room temperature, he has gelled in 3 hours. In the system which added the controlling agent to the microencapsulation platinum catalyst ((D) ingredient) of the comparative example 3, although torque time becomes long 10% rather than the comparative example 1, the time from torque time to 90% torque time is very long, and time takes 10% too much by the end of hardening. On the other hand, in the working example 1, pot life becomes long rather than the comparative example 1, and it turns out that the time to the end of hardening becomes short, and long pot life and the prompt hardening characteristic are obtained. In this case, the constituent it has a constituent and the pot life to desire and hardening speed with the concentration of a microencapsulation platinum catalyst ((D) ingredient), the addition of the controlling agent ((F) ingredient) added later, and the addition of a platinum catalyst ((E) ingredient) can be obtained.

[0068] Next, 120 ** and the curing conditions for 20 minutes compared the working examples 2, 3, and 4 and the comparative example 4 with sponge-like foam in the state of the cell after carrying out hardening foaming. A result is shown in Table 2.

[0069]

[Table 2]

	実施例 2	実施例 3	比較例 4	実施例 4
硬化前状態	微小発泡あり	微小発泡あり	発泡なし	微小発泡あり
硬化後のセル状態	1mm 以下 (セルは微小で均一であった)	1mm 以下 (セルは微小で均一であった)	2mm 以上 (セルは大きくかつ不均一であった)	1mm 以下 (セルは微小で均一であった)

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention]This invention relates to the organopolysiloxane constituent excellent in preservability and hardenability.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention]Preservability and hardenability are [organopolysiloxane constituent of this invention] compatible.
[0045]

[Translation done.]

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TECHNICAL PROBLEM

[Description of the Prior Art]From before, the addition reaction by the platinum metal catalyst of an aliphatic unsaturated group and a hydrosilyl group is used for many fields, and especially a platinum compound, It is used as a catalyst compound with the highest flexibility in these fields, and is used for organic synthesis reactions, such as composition of a sill alkane bond, and also especially in the field of silicone industry, It is used as a means of bridge construction of addition reaction type resin or rubber, and is used for the use of extrusion by adhesives, a coating agent, a potting agent, gel, foam, and liquefied or millable rubber, compression molding, or injection molding as a concrete use. [0003]In recent years, in the field of silicone industry, the material which a retention period hardens for a long time and promptly from a viewpoint of processability and workability is called for, and many are proposed about the constituent which used the addition reaction by platinum metal catalyst use as a bridge construction system for this reason. Many technology about the controlling agent for controlling the shelf life of a platinum metal catalyst and pot life in connection with this is also indicated, For example, a benzotriazol system compound (JP,S40-25069,B), An acetylene alcohol system compound (JP,S44-31476,B), A vinyl group content polysiloxane compound (JP,S48-10947,B), hydroperoxide (JP,S57-20340,B), an amine compound (JP,S63-56563,A), etc. are proposed.

[0004] The method by such chemical control has a limit in the balance of working life and a cure rate, and it is becoming impossible however, to be unable to cope with the market demand currently asked for still longer preservability and sharp hardenability.

[0005]Then, embedding of the platinum metal catalyst is carried out to thermoplastics, silicone resin, etc. which have the specific melting point, it is encapsulated, it blends into a constituent, and the method of making a platinum metal catalyst emit into a silicone composition by the dissolution by melting of these resin by heating or a solvent is proposed. As a prior art reference about this technology, for example JP,S49-134786,A, There are JP,S58-37053,A, JP,S64-51140,A, JP,H2-9448,A, JP,H2-14244,A, JP,H5-202193,A, JP,H7-196921,A, etc.

[0006]However, since a high-concentration platinum metal catalyst is unevenly distributed and exists in a constituent, the method by this microencapsulation has the problem of being easy to cause partial hardening.

[0007]Then, in order to solve the problem of this point, the methods (JP,H4-46962,A etc.) of using acetylene alcohol etc. as an reaction inhibitor are proposed, and preventing a partial hardening reaction is indicated.

[0008]However, when this constituent was also developed for various uses, it became clear that some faults arose.

[0009]For example, when adding adhesion components to these constituents and using as heat cure type silicone rubber adhesives, The temperature setting in a mass-production line is comparatively low, and if fixed time is taken for the thermoplastics etc. which are carrying out embedding of the platinum metal catalyst to dissolve, the problem to which hardening and adhesion in a factory line

become imperfect will sometimes arise. When blending hydroxyl supply sources, such as alcohol or water, with a constituent and obtaining foam in a heating line, it is known that foaming by a little dehydrogenation in early stages of a reaction will serve as the core, and good foam will be obtained, but. The above-mentioned reaction inhibitor also controls this initial foaming, and there is a problem of being unable to obtain good foam. When using it as an addition hardening material of a millable type and it vulcanizes at high speed in order to mold an electric wire, a tube, etc., a tack (feeling of adhesion) remains in the surface, and there are problems -- the molding body which has the smooth surface is not obtained.

[0010]Therefore, an object of this invention is to provide the organopolysiloxane constituent which solved the above-mentioned problem.

[0011]

[The means for solving a technical problem and an embodiment of the invention] As opposed to the organopolysiloxane constituent which contains organopolysiloxane containing an alkenyl group or a hydroxyl group, and the ORGANO hydrogen polysiloxane as a result of inquiring wholeheartedly, in order that this invention person may attain the above-mentioned purpose, (D) Thermoplastic organic resin, thermoplastic silicone resin whose melting point or softening temperature is 40-200 **, A molecular weight to the whole quantity of a constituent as a platinum metal catalyst platinum metal atom by which embedding was carried out by either which is chosen from 1,000 or less heat colligative compound And 1-1,000 ppm, (E) Use together in the quantity which supplies the platinum metal atom of the quantity of 1/10 or less weight of the platinum metal atom supplied from the platinum metal catalyst (D) ingredient by which embedding is not carried out with thermoplastics etc., and. By blending an addition reaction depressant, excel in preservability, and working life is long, and. The problem which hardenability was good, hardened promptly at the time of heat cure, and moreover mentioned above, namely, the case where it takes time when the temperature setting in a mass-production line is comparatively low, and it is fixed although the thermoplastics etc. which carry out embedding of the platinum metal catalyst dissolve when adhesion components are added and it uses as heat cure type silicone rubber adhesives -- the problem that hardening and adhesion are imperfect in these factory lines. When hydroxyl supply sources, such as alcohol or water, are used together to the above-mentioned constituent and foam is too made profitably like in a heating line as foam, The difficulty of initial foaming not being controlled, either and being unable to obtain good foam, When molding an electric wire and a tube in the addition hardening material of a millable type, and vulcanization at a high speed was performed, the tack (feeling of adhesion) remained in the surface, and the knowledge of the ability to solve difficulties -- the smooth surface cannot be obtained -- was carried out.

[0012]Namely, according to this invention, protect with thermoplastics etc. 90weight % or more of the platinum metal catalyst of the quantity which an addition reaction completes by within a time [fixed] on a design (as a platinum metal atomic weight), and control the change at the time of preservation, and. Coexistence with preservability and hardenability can be aimed at by considering it as the reaction control system by the chemistry coordination conventionally used in the state where embedding of 10 or less weight % of a platinum metal catalyst is not carried out with thermoplastics etc. (as a platinum metal atomic weight).

[0013]Therefore, organopolysiloxane 100 weight section this invention is indicated to be with the (A) following general formula (1), (B) ORGANO hydrogen polysiloxane 0.1 shown with the following general formula (2) which has in a molecule the hydrogen atom combined with at least three silicon atoms - 50 weight section, (C) Thermoplastic organic resin whose zero to compound 20 weight section which has an active hydrogen group, (D) melting point, or softening temperature is 40-200 **, Thermoplastic silicone resin and platinum metal catalyst to which embedding of the molecular weight was carried out by either which is chosen from 1,000 or less heat colligative compound As a platinum metal atom, to the whole quantity of a constituent 1-1,000 ppm, (E) The quantity which supplies the platinum metal atom of the quantity of 1/10 or less weight of the platinum metal atom

supplied from a platinum metal catalyst (D) ingredient, (F) Contain 0.001 to addition reaction depressant 20 weight section, and (G) bulking agent 0 - 1,000 weight section, and provide the organopolysiloxane constituent characterized by things.

[0014]

[Chemical formula 3]



R^1 in formula and X -- the alkyl group of the carbon numbers 1-10, and an aryl group. [however,] an aralkyl group, an alkenyl group, the basis by which some hydrogen atoms combined with the carbon atom of these bases were replaced with the halogen atom and the basis chosen from a hydroxyl group, and k show four or more integers -- the inside of R^1 and the whole quantity of X -- an alkenyl group and/or a hydroxyl group -- 0.001-1-mol % -- it contains.

[0015]

[Chemical formula 4]



however, R^2 in formula -- the alkyl group of the carbon numbers 1-10, and an aryl group. As for an aralkyl group and the basis for which some hydrogen atoms combined with the carbon atom of these bases are chosen from the univalent basis replaced with the halogen atom, the atom which is chosen from a hydrogen atom and R^2 as for Y or a univalent basis, and m, zero or more integers and $m+n$ of one or more integers and n are the integers of 3-500.

[0016] If lessons is taken from this invention and it explains in more detail hereafter, as mentioned above, organopolysiloxane will be used for the organopolysiloxane constituent of this invention as a (A) ingredient. This (A) ingredient is base polymer of this constituent, is organopolysiloxane of straight chain shape fundamentally, and is shown by the following general formula (1).

[0017]

[Chemical formula 5]



[0018] Here, the above-mentioned R^1 and X are the carbon numbers 1-10, the alkyl group of 1-8, an aryl group, an aralkyl group, an alkenyl group and the basis by which some hydrogen atoms on the carbon atom of these bases were replaced with the halogen atom, and a basis chosen from a hydroxyl group preferably. Specifically A methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, An isobutyl group, a tert-butyl group, a pentyl group, a hexyl group, a cyclohexyl group, Alkyl groups, such as an octyl group, a nonyl group, and a decyl group, a vinyl group, an allyl group, Alkenyl groups, such as a propenyl group, an isopropenyl group, a butenyl group, and a hexenyl group, Although halogenated hydrocarbon groups, such as aralkyl groups, such as aryl groups, such as a phenyl group and a tolyl group, benzyl, and a phenylethyl group, a chloromethyl group, a bromoethyl group, and a 3,3,3-trifluoropropyl group, and a hydroxyl group can be illustrated, it is not limited to these. In this case, although R^1 and X may be mutually the same or

it may differ, it is [R^1 and 0.001–1 mol% of the whole quantity of X] especially required for 0.02–0.8–mol % to be an alkenyl group and/or a hydroxyl group. If they are a functional group which contributes to crosslinking reaction, their intensity of a hardened material is weak when an alkenyl group and a hydroxyl group have less the quantity than 0.001–mol %, and they become a thing without intensity, and do not function as a rubber elastomer and there are than 1–mol %, they will become what has a hardened material high crosslinking density and weak. [more] As for a hydroxyl group, it is preferred to have combined only with the silicon atom of chain both ends as a functional group which contributes to crosslinking reaction, and an alkenyl group, Even if it has combined with which silicon atom in the middle of chain both ends or a chain, it has combined with both, but it is preferred that it is what contains the alkenyl group combined with the silicon atom of chain both ends at least in respect of the physical properties of a hardened material, etc. As for X, it is [a vinyl group or a hydroxyl group, and R^1] preferred from points, such as the ease of carrying out of acquisition, and cost, to be chosen from a methyl group, a phenyl group, a 3,3,3-trifluoropropyl group, and a vinyl group.

[0019]A hardened material becomes it weak preferably that it is 100 or more integers and k is three or less still more preferably 50 or more four or more, and k cannot be used as a molding body. in addition -- although the maximum in particular of k is not restricted -- usually -- 15,000 -- it may be about 8,000 preferably, and organopolysiloxane of this invention may be the shape of liquid, and paste state, or may be crude rubber-like.

[0020]The (B) ingredient of this invention is the ORGANO hydrogen polysiloxane shown with a following general formula (2), and acts as a cross linking agent or a cross linking agent and foaming agent.

[0021]

[Chemical formula 6]



[0022] here -- the above-mentioned R^2 -- the carbon numbers 1–10 -- desirable -- the alkyl group of 1–8. Some hydrogen atoms on the carbon atom of an aryl group, aralkyl groups, and these bases are the bases chosen from the univalent basis replaced with the halogen atom, and Y is the atom or the univalent basis chosen from a hydrogen atom and R^2 . Although the same thing as what was illustrated in R^1 as an alkyl group, an aryl group, an aralkyl group, and a halogenated hydrocarbon group here in R^2 or Y can be illustrated, It is preferred that it is what does not contain an aliphatic unsaturated group as this R^2 or Y, and this ORGANO hydrogen polysiloxane needs in a molecule to have the hydrogen atom (namely, SiH group) combined with at least three silicon atoms. n -- zero or more -- desirable -- 0–499 -- the integer of 0–199 is shown still more preferably -- m -- one or more -- desirable -- 3–500 -- the integer of 4–200 is shown still more preferably -- the value of n+m -- 3–500 -- it is an integer of 4–200 preferably.

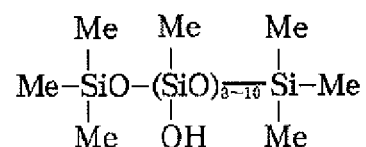
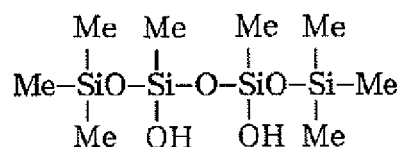
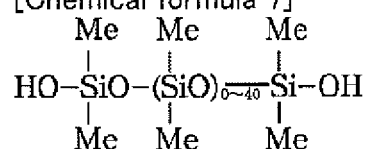
[0023]. The above-mentioned (B) ingredient is a cross linking agent reacted to the above-mentioned (A) ingredient. [(that is, an alkenyl group in the (A) ingredient and a SiH group in the (B) ingredient add by hydrosilylation, or a silanol group in the (A) ingredient and a SiH group in the (B) ingredient add by dehydrogenation), and] The (C) ingredient and dehydrogenation of an optional component which are mentioned later are caused, it acts also as a foaming agent, and especially the loadings need to carry out 1–25 weight-section combination 0.1 to 50 weight section to base polymer 100 weight section of the (A) ingredient. When there are few loadings than 0.1 weight sections, bridge construction fully becomes impossible, and if more than 50 weight sections, or bridge construction becomes impossible too. [weatherability]

[0024] A hydroxyl group (namely, silanol group) which the (A) ingredient combined with a silicon atom is not contained, And in not blending the (C) ingredient mentioned later (it is not necessary to make a constituent foam and to make form or sponge form). (A) To 1 mol of alkenyl groups in an ingredient, the (B) ingredient can also be blended so that a mole ratio of a SiH group in the (B) ingredient may become 0.5–10, especially one to about 5.

[0025] Next, it is a compound which has active hydrogen, when a constituent of this invention is used for the (C) ingredient of this invention as a constituent for foam, it is a required ingredient, but if it is not necessary to make a constituent foam and to make form or sponge form, it can omit the combination. Here, a compound which has active hydrogen means a compound which has a hydrogen atom (for example, hydroxy group) which can carry out dehydration to a SiH group in the (B) ingredient in response to the bottom of existence of a platinum metal catalyst in [at least one] a molecule. Although a publicly known compound can be used as a compound which has active hydrogen, don't deactivate the catalytic activity of a platinum metal catalyst which is (D) and the (E) ingredient which are mentioned later. the carbon numbers 1–20 which specifically have one piece or two OH radicals or more in water and one molecule -- desirable -- about one to 12 alcohol compound. Silang containing a silanol group or 2–50 silicon atoms -- compounds, such as about two to 20 siloxane, preferably, [mention and] What is shown in methanol, ethanol, n-propanol, iso-propanol, butanol, ethylene glycol, a diethylene glycol, glycerin, a trimethyl silanol, diphenylsilanediol, and a following formula is illustrated. These can mix independent or two sorts or more, and can use one sort.

[0026]

[Chemical formula 7]



(Me shows a methyl group.)

[0027] The loadings of the above-mentioned (C) ingredient carry out 0.1–15 weight-section combination 0.1 to 20 weight section, especially when using it as 0 – 20 weight section, especially a constituent for foam to base polymer 100 weight section of the above-mentioned (A) ingredient.

[0028] The (D) ingredient of this invention is the platinum metal catalyst which it *****ed. In this invention, a platinum metal catalyst means platinum metal atoms, such as platinum, palladium, and rhodium, the simple substance of a platinum metal which contains a platinum atom preferably, platinum metal compounds, and those complexes as catalyst metal.

[0029] Although the (D) ingredient of this invention acts as a catalyst for carrying out the addition reaction of the above-mentioned (A) ingredient and the (B) ingredient, In order to raise the preservability of a constituent, it is considered as the platinum metal (that is, it *****ed) catalyst by which embedding was carried out with either [which has the

melting point of 40–200 °C or softening temperature] thermoplastic organic resin, thermoplastic silicone resin and a with a molecular weight of 1,000 or less heat colligative compound. This (D) ingredient can show the activity of a platinum metal catalyst above near the melting point (or softening temperature) of the compound which carries out embedding, and can be contributed to hardening and/or foaming of a constituent. Therefore, although the melting point or softening temperature of the above-mentioned thermoplastic organic resin, thermoplastic silicone resin, and a with a molecular weight of 1,000 or less heat colligative compound is chosen by the use and preservation conditions which use the constituent of this invention, especially in this invention, it requires that it is 50–150 °C at 40–200 °C. The preservability in ordinary temperature is not enough in it being less than 40 °C, and if it exceeds 200 °C, preservability is enough, but the difficulty that hardening takes time arises.

[0030]As thermoplastic organic resin, in this case, polyolefin resin, polystyrene resin, Organic resin other than silicone series, such as an acrylic resin and cellulose type resin, is mentioned, As thermoplastic silicone resin (namely, organopolysiloxane resin of the three-dimensional network structure containing branching structures, such as 3 functionality siloxane units and/or a SiO₂ unit), although selection use of the various things is carried out, The silicone resin which has aliphatic unsaturated groups, such as a phenyl group or a perfluoroalkyl group (for example, 3,3,3-trifluoropropyl group), and an alkenyl group (for example, a vinyl group, an allyl group, a propenyl group), is preferred. A molecular weight 1,000 or less heat colligative compound, Are heat colligative compounds other than the above-mentioned thermoplastic organic resin and thermoplastic silicone resin, and as this heat colligative compound, 2-butene 1,4-diol, diphenylacetylene, 4-hexyl resorcinol, 2-vinylnaphthalene, 2-acetyl-1-tetralone, the 2, 5-diphenyloxazole, 3,6-dichloro pyridazine, 2,5-torr quinone, 3,6-dimethyl- 4-octyne-3,6-diol, Bis(2, 2, 6, and 6-tetramethyl 4-piperidinyl)SEBUKETO, 3,3'-thiodipropionic acid-di-n-octadecyl, 2,4,7,9-tetra-methyl-5-decyne-4,7-diol, 2,5-dimethyl-3-hexyne-2,5-diol, 1,3-bis(trimethylsilyl ethynyl) benzene, a thiocumarone 4-ol, etc. are usable.

[0031]On the other hand as a platinum metal catalyst by which embedding is carried out to the above-mentioned resin or a heat colligative compound, They are platinum metals, such as platinum, rhodium, and palladium, and a catalyst which contains platinum preferably especially, The various complexes etc. which are derived from the platinum black more publicly known than before as an addition reaction catalyst, chloroplatinic acid, or this are mentioned, Specifically, the complex of the denaturing alcohol thing of platinum black, chloroplatinic acid, and chloroplatinic acid, chloroplatinic acid, an olefin, aldehyde, a vinyl siloxane, acetylene, and acetylene alcohol, etc. can be mentioned.

[0032]As such a (D) ingredient, JP,S49-134786,A, As for the silicone resin which can mention the platinum metal catalyst etc. by which embedding was carried out, and is used here by silicone resin which is indicated to JP,H4-46962,A etc., it is preferred that it is a thing having a phenyl group or a perfluoroalkyl group, and an aliphatic unsaturated group. the platinum metal catalyst by which embedding was carried out with the thermoplastic organic resin currently indicated by JP,S64-47442,A, such as polystyrene and polyolefine, as other examples -- further, The molecular weight which does not belong under the category of the above-mentioned thermoplastic organic resin can mention the platinum group compound etc. by which embedding was carried out with 1,000 or less heat colligative compound.

[0033]As a manufacturing method of the platinum metal catalyst by which embedding was especially carried out with the heat colligative compound, Although publicly known methods, such as a method indicated in the gazette etc. which were mentioned above, may be used and it is not restricted in particular, it can obtain by contacting a heat colligative compound and a platinum group compound in fusion or the solution state of a heat colligative compound, for example. The solid catalyst which the platinum metal catalyst distributed uniformly is acquired by heating here more than the melting point of a compound, when performing a thermal melting solution, making a platinum metal catalyst support with the state where it was made to equalize or distribute in a

solvent, when dissolving, cooling or solvent distilling off and solidifying this. In addition, [whether misty state is made to spray and solidify these by the liquid state in fusion or the dissolution, and] Or perform solvent removal and it is made to emulsify with an emulsifier by the method by the spray dry which obtains particles, and underwater, and it cools below to the solidification temperature of a solvent, dissolving in the method and solvent which acquire a solid catalyst, and the method of acquiring a solid catalyst with what is called a freeze drying method etc. that perform solvent removal under decompression, etc. are mentioned. Thus, it may use as a granular material, and it can be again made a slurry or paste state, can be made to be able to distribute by silicone oil, and the acquired solid catalyst can also be used.

[0034]The loadings of the above-mentioned (D) ingredient are the quantity supplied 1–1,000 ppm as a platinum metal atom to the constituent whole quantity, and a quantity preferably set to 5–200 ppm.

[0035]The (E) ingredient of this invention is a platinum metal catalyst, and this uses platinum metal catalyst itself by which shows the meaning mentioned above and embedding is not carried out to thermoplastic organic resin, thermoplastic silicone resin, and a heat colliquative compound. This complements the function as an addition reaction catalyst of the above-mentioned (D) ingredient, specifically makes an initial set and initial foaming good, and when it fabricates an electric wire, a tube, etc. with which especially high-speed vulcanization is performed, it can cancel the surface tackiness (feeling of adhesion) etc. which pose a problem.

[0036]A publicly known platinum metal catalyst can be conventionally used for the above-mentioned (E) ingredient, and, unlike the above-mentioned (D) ingredient, a platinum metal catalyst, Without carrying out embedding with thermoplastics, thermoplastic silicone resin, and a heat colliquative compound, as mentioned above as it is, It is blended into a constituent and the complex of the denaturing alcohol thing of platinum black, chloroplatinic acid, and chloroplatinic acid, chloroplatinic acid, an olefin, aldehyde, a vinyl siloxane, acetylene, and acetylene alcohol, etc. can specifically be illustrated.

[0037]The quantity of the platinum metal atom in the (E) ingredient the loadings of the above-mentioned (E) ingredient by a weight ratio to the quantity of the platinum metal atom supplied from the above-mentioned (D) ingredient 1/10 or less. 1/20 or less is used preferably -- the weight ratio of the above [the minimum] -- 1/100,000 (0.001%) -- desirable -- 1/1,000 (0.1%) -- it is especially 1/100 (1%). When there are too many additions, it becomes impossible to hold the balance of preservability and hardenability. When there are too few additions, the effect by concomitant use of the (D) ingredient and the (E) ingredient may not be acquired.

[0038]Although the addition reaction depressant which is the (F) ingredient of this invention can be used in order to control the reaction by the platinum metal atom supplied from the above-mentioned (E) ingredient, and a thing more publicly known than before can be used, Specifically A benzotriazol system compound (JP,S40-25069,B), An acetylene alcohol system compound (JP,S44-31476,B), A vinyl group content polysiloxane compound (JP,S48-10947,B), It can choose from hydroperoxide (JP,S57-20340,B), an amine compound (JP,S63-56563,A), etc., and can choose from acetylene or an acetylene alcohol content compound suitably. 3-methyl-1-butyne-3-ol, 3-methyl-1-pentyne-3-ol, ethynylcyclohexanol, 3,5-dimethyl-1-hexyne-3-ol, etc. can more specifically be mentioned.

[0039]Although the loadings of the above-mentioned (F) ingredient change with the structure of the (F) ingredient, and molecular weights, In this invention, to above-mentioned (A) ingredient 100 weight section, 0.001 – 20 weight section, It is preferred that it is the quantity which turns into 2–500 Eq especially about 1–1,000 Eq to the platinum metal atom which is preferably made into the range of 0.002 to 5 weight section, and is fundamentally supplied as a (E) ingredient.

[0040]Bulking agents which are the (G) ingredients of this invention are the arbitrary ingredients added for increase in quantity of a constituent or reinforcement of physical intensity and also flameproofing, thermal conductivity, and electrical conductivity, Specifically Haze-like pyrogenic silica, sedimentation nature silica, crystalline grinding silica, colloidal calcium carbonate, What

processed precipitated calcium carbonate, heavy calcium carbonate, acetylene black, furnace carbon, titanium oxide, metal, a metallic oxide, and its surface with a silane compound and a siloxane compound is mentioned. To (A) ingredient 100 weight section, zero to 1,000 weight section, one to 1,000 weight section, loadings of the (G) ingredient are 1 – 400 weight section, and if 1,000 weight sections are exceeded, combination is difficult, or its hardened material is weak and they become what was remarkably inferior in a mechanical property especially preferably.

[0041]Although the constituent of this invention can blend (A) – (G) ingredient mentioned above, A thixotropic improver which can also blend a publicly known additive agent if needed, and is specifically used in this industry as these additive agents, Silicone oil as an adhesive improver and a plasticizer, $R_3SiO_{1/2}$ unit for intensity reinforcement, and a SiO_2 unit are made into basic structure. Silicone resin including structure where silicone resin or essential structure to contain are $RSiO_{3/2}$ unit can be added unless the purpose of this invention is checked (each R here.).

Monovalent hydrocarbon radicals, such as an alkyl group of the carbon numbers 1–8, an alkenyl group, and an aryl group, are shown.

[0042]In this case, as an adhesive improver, the carbon functional silane or siloxane which has a reactant group is effective, For example, gamma-glycidoxypyrtrimetoxysilane, gamma-acryloxypropyltrimethoxysilane, Epoxy functional groups, such as gamma-methacryloxypropyl trimethoxy silane, The alkoxy silane which has reactant groups, such as an acrylic functional group (bird), and its partial hydrolysis condensate, Methyl hydrogen polysiloxane of an end bird alkoxy-silyl-groups blockade, Can use trimethoxysilylpropyl denaturation annular methyl hydrogen polysiloxane, triallyl isocyanurate, etc., and the loadings, (A) They are about 0.01–10 weight sections more preferably 0.01 to 50 weight section zero to 50 weight section to ingredient 100 weight section.

[0043]Although the curing conditions of this invention constituent can be suitably selected in a use, it is usually carried out in the range for about 2 to 120 minutes at 60–150 **.

[Translation done.]

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EXAMPLE

[Working example] Although the synthetic example of a catalyst, an working example, and a comparative example are given and this invention is explained concretely hereafter, this invention is not limited to the following working example. The part in the following example shows a weight section.

[0046][Example 1 of catalyst composition] As a platinum atom, in the 5,000 ppm toluene solution of a siloxane denaturation platinum complex, Tales doses of the phenyl groups and vinyl group content silicone resin containing $C_6H_5SiO_3/2$ unit with a melting point of 78 **, and $(CH_2=CH)SiO_3/2$ unit to toluene are added, It agitated until it became uniform, and the resin powder platinum catalyst (the catalyst 1, a platinum atomic weight: 5,000 ppm) was prepared by the spray-drying method.

[0047][Example 2 of catalyst composition] to 5 g of 3,6-dimethyl- 4-octyne-3,6-diol (melting point of 54 **). The vinyl group content siloxane complex 5g derived from chloroplatinic acid was added, and it heat-treated at 80 ** for 1 hour, and after carrying out a strip, it cooled and the solid hydrosilylation catalyst (the catalyst 2, a platinum atomic weight: 5,000 ppm) was prepared.

[0048][Example 3 of catalyst composition] with 5 g of 1,3-bis(trimethylsilyl ethynyl)benzene (melting point of 58 **). The vinyl group content siloxane complex 5g derived from chloroplatinic acid is added, It heat-treated at 80 ** for 1 hour, and after adding the polyglycerin system surface-active agent 0.5g to this and carrying out emulsification to it underwater, it filtered and dried and the hydrosilylation catalyst (the catalyst 3, a platinum atomic weight: 5,000 ppm) of fine powder form was prepared.

[0049][Working example 1] The viscosity of 25 ** by which chain both ends were blocked with the vinyl dimethylsilyl group 100 copies of dimethylpolysiloxane of 30,000cp, It mixed until the surface put ten copies of haze-like silica of specific surface area [of 130 m] ²/g processed by dichlorosilane into the omnipotent mixer and became uniform, and the base compound was prepared.

[0050]The catalyst 1 acquired in the above-mentioned example 1 of catalyst composition to 100 copies of this base compound 2.0 copies (it is 100 ppm by platinum conversion to said base compound), The toluene solution of the same siloxane denaturation platinum complex as what was used in the example 1 of catalyst composition 0.1 copy (it is 5.0 ppm by platinum conversion to said base compound), And after agitating until it adds 0.002 copy of 2-ethylhexanol and becomes uniform with an omnipotent mixer, Both ends added 16 copies of methyl hydrogen polysiloxane which has the 0.005 mol/g SiH group blocked with the trimethylsilyl group, and were mixed, and the constituent 1 (the weight ratio of the platinum atom in the (E) ingredient to the platinum atom in the (D) ingredient is 0.05%) was obtained.

[0051][Working example 2] The viscosity of 25 ** by which chain both ends were blocked with the vinyl dimethylsilyl group 100 copies of dimethylpolysiloxane of 30,000cp, It mixed until the surface put ten copies of haze-like silica of specific surface area [of 130 m] ²/g processed by dichlorosilane into the omnipotent mixer and became uniform, and the base compound was prepared.

[0052]For water 0.2 copy and the catalyst 1 to 100 copies of this base compound 1.0 copy (it is 50 ppm by platinum conversion to a base compound), The toluene solution of the same siloxane denaturation platinum complex as what was used in the example 1 of catalyst composition 0.01 copy (it is 0.5 ppm by platinum conversion to a base compound), And after agitating until it adds 0.002 copy of 2-ethylhexanol and becomes uniform with an omnipotent mixer, The viscosity of 25 ** by which both ends were blocked with the trimethylsilyl group adds five copies and 0.3 copy of phenylsilane, and mixes methyl hydrogen polysiloxane (the amount of SiH groups is 0.016 mol/g) of 40cp, The constituent 2 (the weight ratio of the platinum atom in the (E) ingredient to the platinum atom in the (D) ingredient is 0.01%) was obtained.

[0053][Working example 3] The viscosity of 25 ** by which chain both ends were blocked with the vinyl dimethylsilyl group 100 copies of dimethylpolysiloxane of 30,000cp, It agitated until the surface put ten copies of haze-like silica of specific surface area [of 130 m] ²/g processed by dichlorosilane into the omnipotent mixer and became uniform, and the base compound was prepared.

[0054]For water 0.2 copy and the catalyst 2 to 100 copies of this base compound 1.0 copy (it is 50 ppm by platinum conversion to a base compound), A toluene solution of the same siloxane denaturation platinum complex as what was used in the example 1 of catalyst composition 0.01 copy (it is 0.5 ppm by platinum conversion to a base compound), And after agitating until it adds 0.002 copy of 2-ethylhexanol and becomes uniform with an omnipotent mixer, Viscosity of 25 ** by which both ends were blocked with a trimethylsilyl group adds five copies and 0.3 copy of phenylsilane, and mixes methyl hydrogen polysiloxane (the amount of SiH groups is 0.016 mol/g) of 40cp, The constituent 3 (a weight ratio of a platinum atom in the (E) ingredient to a platinum atom in the (D) ingredient is 0.01%) was obtained.

[0055]The [comparative example 1] Viscosity of 25 ** by which chain both ends were blocked with a vinyl dimethylsilyl group 100 copies of dimethylpolysiloxane of 30,000cp, It agitated until the surface put ten copies of haze-like silica of specific surface area [of 130 m] ²/g processed by dichlorosilane into an omnipotent mixer and became uniform, and a base compound was prepared.

[0056]2.1-copy (it is 105 ppm by platinum conversion to base compound) addition of the catalyst 1 is carried out to 100 copies of this base compound, After agitating until it became uniform with an omnipotent mixer, both ends added 16 copies of methyl hydrogen polysiloxane which has SiH-group 0.005 mol/g blocked with a trimethylsilyl group, and were mixed, and the constituent 4 was obtained.

[0057][Comparative example 2] The viscosity of 25 ** by which chain both ends were blocked with the vinyl dimethylsilyl group 100 copies of dimethylpolysiloxane of 30,000cp, It agitated until the surface put ten copies of haze-like silica of specific surface area [of 130 m] ²/g processed by dichlorosilane into the omnipotent mixer and became uniform, and the base compound was prepared.

[0058]The toluene solution of the same siloxane denaturation platinum complex as what was used in the example 1 of catalyst composition to 100 copies of this base compound 2.1 copies (it is 105 ppm by platinum conversion to a base compound), And after agitating until it added 0.002 copy of 2-ethylhexanol and became uniform with the omnipotent mixer, both ends added 16 copies of methyl hydrogen polysiloxane which has SiH-group 0.005 mol/g blocked with the trimethylsilyl group, and were mixed, and the constituent 5 was obtained.

[0059][Comparative example 3] The viscosity of 25 ** by which chain both ends were blocked with the vinyl dimethylsilyl group 100 copies of dimethylpolysiloxane of 30,000cp, It agitated until the surface put ten copies of haze-like silica of specific surface area [of 130 m] ²/g processed by dichlorosilane into the omnipotent mixer and became uniform, and the base compound was prepared.

[0060]The catalyst 1 to 100 copies of this base compound 2.1 copies (it is 105 ppm by platinum conversion to a base compound), And after agitating until it added 0.002 copy of 2-ethylhexanol and became uniform with the omnipotent mixer, both ends added 16 copies of methyl hydrogen polysiloxane which has SiH-group 0.005 mol/g blocked with the trimethylsilyl group, and were mixed, and the constituent 6 was obtained.

[0061][Comparative example 4] The viscosity of 25 ** by which chain both ends were blocked with the vinyl dimethylsilyl group 100 copies of dimethylpolysiloxane of 30,000cp, It agitated until the surface put ten copies of haze-like silica of specific surface area [of 130 m] ²/g processed by dichlorosilane into the omnipotent mixer and became uniform, and the base compound was prepared.

[0062]For water 0.2 copy and the catalyst 2 to 100 copies of this base compound 1.01 copies (it is 50.5 ppm by platinum conversion to a base compound), And after agitating until it adds 0.002 copy of 2-ethylhexanol and becomes uniform with an omnipotent mixer, The viscosity of 25 ** by which both ends were blocked with the trimethylsilyl group added five copies and 0.3 copy of phenylsilane, and mixed methyl hydrogen polysiloxane (the amount of SiH groups is 0.016 mol/g) of 40cp, and the constituent 7 was obtained.

[0063][An working example 4] Viscosity of 25 ** by which chain both ends were blocked with a hydroxyl group 100 copies of dimethylpolysiloxane of 20,000cp, It agitated until the surface put ten copies of haze-like silica of specific surface area [of 130 m] ²/g processed by dichlorosilane into an omnipotent mixer and became uniform, and a base compound was prepared.

[0064]For water 0.2 copy and the catalyst 3 to 100 copies of this base compound 1.0 copy (it is 50 ppm by platinum conversion to a base compound), A toluene solution of the same siloxane denaturation platinum complex as what was used in the example 1 of catalyst composition 0.01 copy (it is 0.5 ppm by platinum conversion to a base compound), And after agitating until it adds 0.002 copy of 2-ethylhexanol and becomes uniform with an omnipotent mixer, Viscosity of 25 ** by which both ends were blocked with a trimethylsilyl group added five copies of methyl hydrogen polysiloxane (the amount of SiH groups is 0.016 mol/g) of 40cp, and was mixed, and the constituent 8 (a weight ratio of a platinum atom in the (E) ingredient to a platinum atom in the (D) ingredient is 0.01%) was obtained.

[0065]The following experiments were conducted on the obtained constituents 1-8. First, about an working example 1 and the comparative examples 1, 2, and 3, a difference of hardenability was checked with a curelast meter. A result of measurement is shown in Table 1.

[0066]

[Table 1]

		10 %トルク時間 (min)	90 %トルク時間 (min)	90 %トルク時間－ 10 %トルク時間 (min)
実施例	1	5.0	6.5	1.5
比較例	1	4.2	7.5	3.3
	2	0.8	1.6	0.8
	3	6.0	10.5	4.5

[0067] As shown in Table 1, in the usual microencapsulation platinum catalyst (namely, only (D) ingredient) of the comparative example 1, the time to the end of hardening from the standup of hardening has taken 3 minutes or more. In the system which added a little controlling agents to the platinum catalyst (namely, (E) ingredient) which is not processed [of the comparative example 2], sufficient working life in the part with short time to the standup of hardening and the room temperature was not obtained, but when saved at a room temperature, he has gelled in 3 hours. In

the system which added the controlling agent to the microencapsulation platinum catalyst ((D) ingredient) of the comparative example 3, although torque time becomes long 10% rather than the comparative example 1, the time from torque time to 90% torque time is very long, and time takes 10% too much by the end of hardening. On the other hand, in the working example 1, pot life becomes long rather than the comparative example 1, and it turns out that the time to the end of hardening becomes short, and long pot life and the prompt hardening characteristic are obtained. In this case, the constituent it has a constituent and the pot life to desire and hardening speed with the concentration of a microencapsulation platinum catalyst ((D) ingredient), the addition of the controlling agent ((F) ingredient) added later, and the addition of a platinum catalyst ((E) ingredient) can be obtained.

[0068]Next, 120 ** and the curing conditions for 20 minutes compared the working examples 2, 3, and 4 and the comparative example 4 with sponge-like foam in the state of the cell after carrying out hardening foaming. A result is shown in Table 2.

[0069]

[Table 2]

	実施例 2	実施例 3	比較例 4	実施例 4
硬化前状態	微小発泡あり	微小発泡あり	発泡なし	微小発泡あり
硬化後のセル状態	1mm 以下 (セルは微小で均一であった)	1mm 以下 (セルは微小で均一であった)	2mm 以上 (セルは大きくかつ不均一であった)	1mm 以下 (セルは微小で均一であった)

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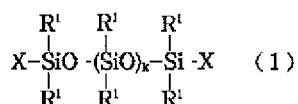
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(54)【発明の名称】 オルガノポリシロキサン組成物

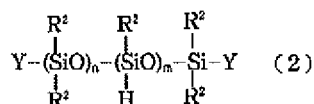
(57)【要約】 (修正有)

【解決手段】 (A)式(1)で示されるオルガノポリシロキサン、(B)式(2)で示されるオルガノハイドロジェンポリシロキサン、(C)活性水素基を有する化合物(任意成分)、(D)融点又は軟化点が40～200℃である熱可塑性有機樹脂、熱可塑性シリコン樹脂、及び分子量が1,000以下の熱融解性化合物から選ばれるいずれかによって包埋された白金族金属触媒、(E)付加反応抑制剤、(F)充填剤を含有してなるオルガノポリシロキサン組成物。



(R¹, R², Xはアルキル基、アリール基、アラルキル基など、kは4以上の整数、R¹, Xの全量中にアルケニル基及び/又は水酸基を0.001～1モル%含有し、Yは水素原子及びR²から選ばれる原子又は1個の

0℃である熱可塑性有機樹脂、熱可塑性シリコン樹脂、及び分子量が1,000以下の熱融解性化合物から選ばれるいずれかによって包埋された白金族金属触媒、(E)付加反応抑制剤、(F)充填剤を含有してなるオルガノポリシロキサン組成物。



基、mは1以上の整数、nは0以上の整数、m+nは3～500の整数。)

【効果】 オルガノポリシロキサン組成物は、保存性と硬化性が両立したものである。

【特許請求の範囲】

【請求項1】 (A) 下記一般式(1)で示されるオルガノポリシロキサン
100重量部、

【化1】



(但し、式中R¹及びXは、炭素数1～10のアルキル基、アリール基、アラルキル基、アルケニル基、及びこれらの基の炭素原子に結合した水素原子の一部がハロゲン原子で置換された基、並びに水酸基から選ばれる基、

kは4以上の整数を示し、R¹及びXの全量中にアルケニル基及び／又は水酸基を0.001～1モル%含有する。)

(B) 分子中に少なくとも3個の珪素原子に結合した水素原子を有する下記一般式(2)で示されるオルガノハイドロジェンポリシロキサン

0.1～50重量部、

【化2】



(但し、式中R²は、炭素数1～10のアルキル基、アリール基、アラルキル基、及びこれらの基の炭素原子に結合した水素原子の一部がハロゲン原子で置換された1

価の基から選ばれる基、Yは水素原子及びR²から選ばれる原子又は1価の基、mは1以上の整数、nは0以上の整数、m+nは3～500の整数である。)

(C) 活性水素基を有する化合物

0～20重量部、

(D) 融点又は軟化点が40～200℃である熱可塑性有機樹脂、熱可塑性シリコーン樹脂、及び分子量が1,000以下の熱融解性化合物から選ばれるいずれかによって包埋された白金族金属触媒

白金族金属原子として組成物の全量に対して1～1,000p

pm、

(E) 白金族金属触媒

(D)成分から供給される白金族金属原子の1/10重量以下の

量の白金族金属原子を供給する量、

(F) 付加反応抑制剤

0.001～20重量部、

(G) 充填剤

0～1,000重量部

を含有してなることを特徴とするオルガノポリシロキサン組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、保存性と硬化性に優れたオルガノポリシロキサン組成物に関する。

【0002】

【従来の技術及び発明が解決しようとする課題】従来より、脂肪族不飽和基とヒドロシリル基との白金族金属触媒による付加反応は多くの分野に利用されており、中でも白金化合物は、これら分野で最も汎用性の高い触媒化合物として使用され、シラルカン結合の合成などの有機合成反応に使用されているほか、特にシリコーン工業の分野で、付加反応型レジンあるいはゴムの架橋の手段として用いられており、具体的な用途としては、接着剤、コーティング剤、ボッティング剤、ゲル剤、発泡

体、液状あるいはミラブルゴムでの押し出し、圧縮成型又は射出成型等の用途に使用されている。

【0003】近年、シリコーン工業の分野においては、加工性、作業性の観点から保存期間が長く、しかも速やかに硬化する材料が求められており、このため白金族金属触媒使用による付加反応を架橋システムとして利用した組成物について数多く提案されている。これに伴い白金族金属触媒のシェルフライフ、ポットライフをコントロールするための制御剤についての技術も数多く開示されており、例えば、ベンゾトリアゾール系化合物(特公昭40-25069号公報)、アセチレンアルコール系化合物(特公昭44-31476号公報)、ビニル基含有ポリシロキサン化合物(特公昭48-10947号公報)、ハイドロパーオキサイド(特公昭57-20340号公報)、アミン系化合物(特開昭63-56563号公報)等が提案されている。

【0004】しかしながら、このような化学的制御による方法は、可使時間と硬化速度とのバランスに限界があり、更に長い保存性とシャープな硬化性が求められている市場要求に対処しきれなくなっている。

【0005】そこで、白金族金属触媒を、特定の融点を有する熱可塑性樹脂やシリコン樹脂などに包埋してカプセル化して組成物中に配合し、加熱によるこれら樹脂の溶融や溶剤による溶解により白金族金属触媒をシリコン組成物中に放出させる方法が提案されている。この技術に関する先行文献としては、例えば、特開昭49-134786号公報、特開昭58-37053号公報、特開昭64-51140号公報、特開平2-9448号公報、特開平2-14244号公報、特開平5-202193号公報、特開平7-196921号公報等がある。

【0006】しかしながら、このマイクロカプセル化による方法は、組成物中に高濃度の白金族金属触媒が偏在して存在するため、部分的な硬化を起こし易いという問題がある。

【0007】そこで、この点の問題を解決するため、アセチレンアルコールなどを反応抑制剤として使用する方法（特開平4-46962号公報等）が提案されており、部分的な硬化反応を防ぐことが記載されている。

【0008】しかしながら、この組成物も種々の用途に展開する場合に幾つかの不具合が生じることが判明した。

【0009】例えば、これらの組成物に接着成分を加えて加熱硬化型シリコンゴム接着剤として用いる場合、連続生産ラインでの温度設定が比較的低く、白金族金属触媒を包埋している熱可塑性樹脂などが融解するのに一定の時間を要すると、生産ラインにおける硬化及び接着が不完全になる問題が時として生じる。また、組成物にアルコールあるいは水などのヒドロキシル基供給源を配合し、加熱ラインにおいて発泡体を得る場合、反応初期の少量の脱水素反応による発泡がその核となって良好な発泡体を得られることが知られているが、上記反応抑制剤がこの初期発泡をも抑制してしまい、良好な発泡体を得ることができないなどの問題がある。更に、ミラブルタイプの付加硬化材料として使用する場合、電線やチューブなどを成型するために高速で加硫を行うと、表面にタック（粘着感）が残り、平滑な表面を有する成型体を得られないなどの問題がある。

【0010】従って、本発明は、上記問題を解決したオ

(A) 下記一般式(1)で示されるオルガノポリシロキサン

(B) 分子中に少なくとも3個の珪素原子に結合した水素原子を有する下記一般式(2)で示されるオルガノハイドロジェンポリシロキサン

(C) 活性水素基を有する化合物

(D) 融点又は軟化点が40～200℃である熱可塑性有機樹脂、熱可塑性シリ

ルガノポリシロキサン組成物を提供することを目的とする。

【0011】

【課題を解決するための手段及び発明の実施の形態】本発明者は上記目的を達成するため鋭意検討を行った結果、アルケニル基又は水酸基を含有するオルガノポリシロキサンとオルガノハイドロジェンポリシロキサンとを含むオルガノポリシロキサン組成物に対し、

(D) 融点又は軟化点が40～200℃である熱可塑性有機樹脂、熱可塑性シリコン樹脂、及び分子量が1,000以下の熱融解性化合物から選ばれるいずれかによって包埋された白金族金属触媒

白金族金属原子として組成物の全量に対して1～1,000ppm、

(E) 熱可塑性樹脂等によって包埋されていない白金族金属触媒

(D) 成分から供給される白金族金属原子の1/10重量以下の量の白金族金属原子を供給する量

で併用すると共に、更に付加反応抑制剤を配合することにより、保存性に優れ、可使時間が長いと共に、硬化性が良好で、加熱硬化時に速やかに硬化し、しかも上述した問題点、即ち接着成分を加え加熱硬化型シリコンゴム接着剤として用いた場合、連続生産ラインでの温度設定が比較的低く、白金族金属触媒を包埋する熱可塑性樹脂などが融解するのに一定の時間がかかる場合にこれらの生産ラインでは硬化及び接着が不完全である問題、また、上記組成物にアルコールあるいは水などのヒドロキシル基供給源を併用し発泡体としてやはり加熱ラインにおいて発泡体を得ようとする場合、初期発泡をも抑制してしまい良好な発泡体を得ることができないなどの難点、更にはミラブルタイプの付加硬化材料において電線やチューブを成型する際、高速での加硫を行った場合に表面にタック（粘着感）が残り平滑な表面を得られないなどの難点を解決し得ることを知見した。

【0012】即ち、本発明によれば、設計上一定の時間内で付加反応が完結する量の白金族金属触媒の90重量%以上（白金族金属原子量として）を熱可塑性樹脂などで保護し、保存時の変化を抑制すると共に、白金族金属触媒の10重量%以下（白金族金属原子量として）を熱可塑性樹脂等によって包埋させない状態で従来用いられてきた化学配位による反応抑制系とすることによって保存性と硬化性との両立を図ることができたものである。

【0013】従って、本発明は、

100重量部、

0、1～50重量部、

0～20重量部、

コーン樹脂、及び分子量が1,000以下の熱融解性化合物から選ばれるいずれかによって包埋された白金族金属触媒

白金族金属原子として組成物の全量に対して1~1,000p

pm、

(E) 白金族金属触媒

(D) 成分から供給される白金族金属原子の1/10重量以下の

量の白金族金属原子を供給する量、

(F) 付加反応抑制剤

0.001~20重量部、

(G) 充填剤

0~1,000重量部

を含有してなることを特徴とするオルガノポリシロキサン組成物を提供する。

【0014】

【化3】



(但し、式中R¹及びXは、炭素数1~10のアルキル基、アリール基、アラルキル基、アルケニル基、及びこれらの基の炭素原子に結合した水素原子の一部がハロゲン原子で置換された基、並びに水酸基から選ばれる基、kは4以上の整数を示し、R¹及びXの全量中にアルケ

ニル基及び／又は水酸基を0.001~1モル%含有する。)

【0015】

【化4】



(但し、式中R²は、炭素数1~10のアルキル基、アリール基、アラルキル基、及びこれらの基の炭素原子に結合した水素原子の一部がハロゲン原子で置換された1価の基から選ばれる基、Yは水素原子及びR²から選ばれる原子又は1価の基、mは1以上の整数、nは0以上の整数、m+nは3~500の整数である。)

【0016】以下、本発明につき更に詳しく説明する

と、本発明のオルガノポリシロキサン組成物は、上述したように、(A)成分としてオルガノポリシロキサンを使用する。この(A)成分は本組成物のベースポリマーであり、基本的に直鎖状のオルガノポリシロキサンで、下記一般式(1)で示される。

【0017】

【化5】

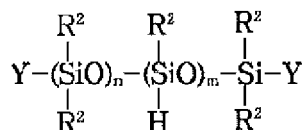


【0018】ここで、上記R¹及びXは、炭素数1~10、好ましくは1~8のアルキル基、アリール基、アラルキル基、アルケニル基、及びこれらの基の炭素原子上の水素原子の一部がハロゲン原子で置換された基、並びに水酸基から選ばれる基である。具体的には、メチル基、エチル基、プロピル基、イソプロピル基、ブチル基、イソブチル基、tert-ブチル基、ペンチル基、ヘキシル基、シクロヘキシル基、オクチル基、ノニル基、デシル基等のアルキル基、ビニル基、アリル基、プロペニル基、イソプロペニル基、ブテニル基、ヘキセニル基等のアルケニル基、フェニル基、トリル基等のアリール基、ベンジル基、フェニルエチル基等のアラルキル基、クロロメチル基、プロモエチル基、3,3,3-トリフルオロプロピル基等のハロゲン化炭化水素基、水酸基を例示することができるが、これらに限定されるもの

ではない。この場合、R¹とXは互いに同一であっても異なってもよいが、R¹及びXの全量の0.001~1モル%、特に0.02~0.8モル%がアルケニル基及び／又は水酸基であることが必要である。アルケニル基及び水酸基は架橋反応に寄与する官能基で、その量が0.001モル%より少ないと、硬化物の強度が弱く、強度のないものになって、ゴム弾性体として機能せず、また1モル%より多いと、架橋密度が高く、硬化物が脆いものになってしまう。なお、架橋反応に寄与する官能基として、水酸基は分子鎖両末端の珪素原子にのみ結合していることが好ましく、またアルケニル基は、分子鎖両末端あるいは分子鎖途中のいずれの珪素原子に結合しているものであっても、また両方に結合しているものであってもよいが、硬化物の物性等の点で、少なくとも分子鎖両末端の珪素原子に結合したアルケニル基を含

有するものであることが好ましい。なお、入手のし易さ、コスト等の点から、Xはビニル基又は水酸基、R¹はメチル基、フェニル基、3, 3, 3-トリフルオロプロピル基、ビニル基から選択されることが好ましい。

【0019】また、kは4以上、好ましくは50以上、更に好ましくは100以上の整数であり、kが3以下であると硬化物が脆くなり、成型体として使用し得ない。なお、kの上限は特に制限されないが、通常15, 00



【0022】ここで、上記R²は、炭素数1~10、好ましくは1~8のアルキル基、アリール基、アラルキル基、及びこれらの基の炭素原子上の水素原子の一部がハロゲン原子で置換された1個の基から選ばれる基であり、Yは水素原子及びR²から選ばれる原子又は1個の基である。ここでR²あるいはYにおいてはアルキル基、アリール基、アラルキル基、ハロゲン化炭化水素基としては、R¹において例示したものと同一ものを例示することができるが、このR²あるいはYとしては脂肪族不飽和基を含有しないものであることが好ましく、またこのオルガノハイドロジェンポリシロキサンは、分子中に少なくとも3個の珪素原子に結合した水素原子（即ち、SiH基）を有することが必要である。また、nは0以上、好ましくは0~499、更に好ましくは0~199の整数を示し、mは1以上、好ましくは3~500、更に好ましくは4~200の整数を示し、n+mの値は3~500、好ましくは4~200の整数である。

【0023】上記（B）成分は、上記（A）成分と反応する架橋剤である（即ち、（A）成分中のアルケニル基と（B）成分中のSiH基がヒドロシリル化により付加するか、あるいは（A）成分中のシラノール基と（B）成分中のSiH基が脱水素反応により付加する）と共に、後述する任意成分の（C）成分と脱水素反応を起こして発泡剤としても作用するもので、その配合量は（A）成分のベースポリマー100重量部に対して、0.1~50重量部、特に1~25重量部配合することが必要である。配合量が0.1重量部より少ないと架橋が十分にできなくなり、50重量部より多いと耐候性に劣ったり、やはり架橋ができなくなる。

【0024】なお、（A）成分が珪素原子に結合した水酸基（即ち、シラノール基）を含有せず、かつ、後述する（C）成分を配合しない（組成物を発泡させてフォーム又はスポンジを形成させる必要がない）場合には、

（A）成分中のアルケニル基1モルに対して、（B）成分中のSiH基のモル比が0.5~10、特に1~5程度になるように（B）成分を配合することもできる。

【0025】次に、本発明の（C）成分は、活性水素を有する化合物であって、本発明の組成物を発泡体用組成

物として用いる際に必要な成分であるが、組成物を発泡させてフォーム又はスポンジを形成させる必要がなければその配合を省略し得る。ここで、活性水素を有する化合物とは、白金族金属触媒の存在下に（B）成分中のSiH基と反応して脱水素し得る水素原子（例えばヒドロキシ基）を分子中に少なくとも1個有する化合物を意味する。活性水素を有する化合物としては公知の化合物を使用することができるが、後述する（D）、（E）成分である白金族金属触媒の触媒活性を失活させるものであってはならない。具体的には、水、1分子中に1個又は2個以上のOH基を有する炭素数1~20、好ましくは1~12程度アルコール化合物、シラノール基を含むシラン又はケイ素原子数2~50、好ましくは2~20程度のシロキサンなどの化合物が挙げられ、メタノール、エタノール、n-プロパノール、iso-プロパノール、ブタノール、エチレングリコール、ジエチレングリコール、グリセリン、トリメチルシラノール、ジフェニルシランジオール及び下記式に示すものなどが例示される。これらは1種を単独で又は2種以上を混合して用いることができる。

【0020】本発明の（B）成分は、下記一般式（2）で示されるオルガノハイドロジェンポリシロキサンで、架橋剤あるいは架橋剤兼発泡剤として作用する。

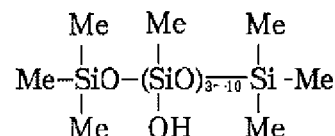
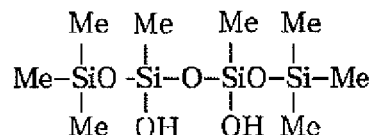
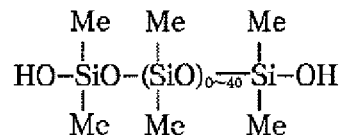
【0021】

【化6】

（2）

【0026】

【化7】



（Meはメチル基を示す。）

【0027】上記(C)成分の配合量は、上記(A)成分のベースポリマー100重量部に対して0~20重量部、特に発泡体用組成物として使用する場合は0.1~20重量部、特に0.1~15重量部配合するものである。

【0028】本発明の(D)成分は、マイクロカプセル化された白金族金属触媒である。なお、本発明において、白金族金属触媒とは、触媒金属として、白金、パラジウム、ロジウム等の白金族金属原子、好ましくは白金原子を含有する、白金族金属の単体、白金族金属化合物及びそれらの錯体を意味する。

【0029】本発明の(D)成分は、上記(A)成分と(B)成分とを付加反応させるための触媒として作用するものであるが、組成物の保存性を向上させるため、40~200℃の融点もしくは軟化点を有する熱可塑性有機樹脂、熱可塑性シリコン樹脂、及び分子量1,000以下の熱融解性化合物のいずれかにて包埋された(即ち、マイクロカプセル化された)白金族金属触媒とするものである。この(D)成分は、包埋する化合物の融点(又は軟化点)付近以上で白金族金属触媒の活性を示し、組成物の硬化及び/又は発泡に寄与することができる。従って、上記熱可塑性有機樹脂、熱可塑性シリコン樹脂、分子量1,000以下の熱融解性化合物の融点又は軟化点は、本発明の組成物を使用する用途及び保存条件によって選択されるが、本発明においては40~200℃、特に50~150℃であることを要する。40℃未満であると常温での保存性が十分ではなく、また200℃を超えると保存性は十分であるが硬化に時間がかかるという難点が生じる。

【0030】この場合、熱可塑性有機樹脂としては、ポリオレフィン樹脂、ポリスチレン樹脂、アクリル樹脂、セルロース系樹脂等のシリコン系以外の有機樹脂が挙げられ、熱可塑性シリコン樹脂(即ち、3官能性シロキサン単位及び/又はSiO₂単位等の分岐構造を含有する三次元網状構造のオルガノポリシロキサンレジン)としては、種々のものが選択使用されるが、フェニル基又はパーフルオロアルキル基(例えば3,3,3-トリフルオロプロピル基)とアルケニル基(例えばビニル基、アリル基、プロペニル基)等の脂肪族不飽和基を有するシリコン樹脂が好ましい。また、分子量が1,000以下の熱融解性化合物は、上記熱可塑性有機樹脂及び熱可塑性シリコン樹脂以外の熱融解性化合物であり、この熱融解性化合物としては、2-ブチン-1,4-ジオール、ジフェニルアセチレン、4-ヘキシルレゾルシン、2-ビニルナフタレン、2-アセチル-1-テトラロン、2,5-ジフェニルオキサゾール、3,6-ジクロロピリダジン、2,5-トルキノン、3,6-ジメチル-4-オクチン-3,6-ジオール、ビス(2,2,6,6-テトラメチル-4-ピペリジニル)セブケート、3,3'-チオジプロピオン酸-ジ-n-オクタ

デシル、2,4,7,9-テトラメチル-5-デシン-4,7-ジオール、2,5-ジメチル-3-ヘキシン-2,5-ジオール、1,3-ビス(トリメチルシリルエチニル)ベンゼン、チオクマロン-4-オールなどが使用可能である。

【0031】一方、上記樹脂あるいは熱融解性化合物に包埋される白金族金属触媒としては、白金、ロジウム、パラジウム等の白金族金属、特に好ましくは白金を含有する触媒であり、従来より付加反応触媒として公知の白金ブラック、塩化白金酸やこれより誘導される各種錯体などが挙げられ、具体的には白金ブラック、塩化白金酸、塩化白金酸のアルコール変性物、塩化白金酸とオレフィン、アルデヒド、ビニルシロキサン、アセチレン、アセチレンアルコール類等との錯体などを挙げるができる。

【0032】このような(D)成分としては、特開昭49-134786号公報、特開平4-46962号公報等に記載されているようなシリコン樹脂で包埋された白金族金属触媒などを挙げることができ、ここで使用されるシリコン樹脂はフェニル基あるいはパーフルオロアルキル基と脂肪族不飽和基を併せ持つものであることが好ましい。その他の例としては、特開昭64-47442号公報に開示されているポリスチレンやポリオレフィンなどの熱可塑性有機樹脂で包埋された白金族金属触媒、更には、上記熱可塑性有機樹脂の範疇に属さない分子量が1,000以下の熱融解性化合物で包埋された白金族化合物などを挙げるができる。

【0033】特に、熱融解性化合物にて包埋された白金族金属触媒の製造方法としては、上述した公報などに記載された方法など公知の方法でよく、特に制限されるものではないが、例えば熱融解性化合物と白金族化合物とを熱融解性化合物の融解あるいは溶解状態にて接触させることによって得ることができる。ここで、熱融解を行う場合は化合物の融点以上に加熱し、溶解を行う場合には溶媒中にて均一化あるいは分散させた状態で白金族金属触媒を担持させ、これを冷却又は溶媒留去して固体化することにより、白金族金属触媒が均一に分散した固体触媒が得られる。その他、融解あるいは溶解での液体状態でこれらを霧状に噴霧し固化させるか、あるいは溶媒除去を行い、微粒子を得るスプレードライによる方法、水中で乳化剤によって乳化させ、固体触媒を得る方法、溶媒に溶解したまま溶媒の固化温度以下に冷却し、減圧下で溶媒除去を行ういわゆる凍結乾燥法等によって固体触媒を得る方法などが挙げられる。このようにして得られた固体触媒は、粉体として用いてもよく、シリコンオイルで再度スラリー又はペースト状にして分散させて用いることもできる。

【0034】上記(D)成分の配合量は、組成物全量に対して白金族金属原子として1~1,000ppm供給される量、好ましくは5~200ppmとなる量であ

る。

【0035】本発明の(E)成分は白金族金属触媒で、これは上述した意味を示し、熱可塑性有機樹脂、熱可塑性シリコン樹脂、熱融解性化合物に包埋されない、白金族金属触媒それ自体を用いるものである。これは、上記(D)成分の付加反応触媒としての機能を補完するもので、具体的には初期硬化、初期発泡を良好にし、特に高速加硫が行われる電線、チューブなどを成形する際に問題となっている表面タック(粘着感)等を解消することができる。

【0036】上記(E)成分は、従来公知の白金族金属触媒を使用することができ、上記(D)成分とは異なり、白金族金属触媒は、上述したように熱可塑性樹脂、熱可塑性シリコン樹脂、熱融解性化合物によって包埋されることなく、そのまま、組成物中に配合されるものであり、具体的には白金ブラック、塩化白金酸、塩化白金酸のアルコール変性物、塩化白金酸とオレフィン、アルデヒド、ビニルシロキサン、アセチレン、アセチレンアルコール類等との錯体などを例示することができる。

【0037】上記(E)成分の配合量は、(E)成分中の白金族金属原子の量が上記(D)成分から供給される白金族金属原子の量に対して重量比で1/10以下、好ましくは1/20以下とされ、その下限は前記の重量比で1/100,000(0.001%)、好ましくは1/1,000(0.1%)、特に1/100(1%)である。添加量が多すぎると保存性と硬化性のバランスを保持できなくなる。また、添加量が少なすぎる場合には、(D)成分と(E)成分の併用による効果が得られない場合がある。

【0038】本発明の(F)成分である付加反応抑制剤は、上記(E)成分より供給される白金族金属原子による反応を制御する目的で使用するので、従来より公知のものを使用することができるが、具体的にはベンゾトリアゾール系化合物(特公昭40-25069号公報)、アセチレンアルコール系化合物(特公昭44-31476号公報)、ビニル基含有ポリシロキサン化合物(特公昭48-10947号公報)、ハイドロパーオキシド(特公昭57-20340号公報)、アミン系化合物(特開昭63-56563号公報)などの中から選択することができ、好適にはアセチレンあるいはアセチレンアルコール含有化合物から選択することができる。より具体的には3-メチル-1-ブチン-3-オール、3-メチル-1-ペンチン-3-オール、エチニルシクロヘキサノール、3,5-ジメチル-1-ヘキシン-3-オールなどを挙げることができる。

【0039】上記(F)成分の配合量は、(F)成分の構造、分子量によって異なるが、本発明においては、上記(A)成分100重量部に対し、0.001~20重量部、好ましくは0.002~5重量部の範囲とされ、基本的には(E)成分として供給される白金族金属原子

に対して1~1,000当量程度、特に2~500当量になる量であることが好ましい。

【0040】本発明の(G)成分である充填剤は、組成物の増量あるいは物理的強度の補強、更には難燃化、熱伝導性、電気伝導性のために加えられる任意の成分で、具体的には煙霧状焼成シリカ、沈降性シリカ、結晶性粉砕シリカ、コロイダル炭酸カルシウム、沈降炭酸カルシウム、重質炭酸カルシウム、アセチレンブラック、ファーネスカーボン、酸化チタン、金属、金属酸化物及びその表面をシラン化合物、シロキサン化合物で処理したもののなどが挙げられる。また、(G)成分の配合量は、

(A)成分100重量部に対し、0~1,000重量部、特に1~1,000重量部、好ましくは1~400重量部であり、1,000重量部を超えると配合が困難であったり、硬化物が脆く、機械的特性が著しく劣ったものになる。

【0041】本発明の組成物は、上述した(A)~(G)成分を配合し得るものであるが、更に必要に応じて公知の添加剤を配合することもでき、これら添加剤として具体的には当業界で用いられるチクソ性向上剤、接着性向上剤、可塑剤としてのシリコンオイル、強度補強のための $R_3SiO_{1/2}$ 単位及び SiO_2 単位を基本構造として含有するシリコンレジンあるいは基本的構造が $RSiO_{3/2}$ 単位である構造を含むシリコンレジンなどを本発明の目的を阻害しない限り添加することができる(ここでRはいずれも、炭素数1~8のアルキル基、アルケニル基、アリール基等の1価炭化水素基を示す)。

【0042】この場合、接着性向上剤としては、反応性基を有するカーボンファンクショナルシラン又はシロキサンが有効であり、例えばγ-グリシドキシプロピルトリメトキシシラン、γ-アクリロキシプロピルトリメトキシシラン、γ-メタクリロキシプロピルトリメトキシシラン等のエボキシ官能性基、アクリル官能性基などの反応性基を有する(トリ)アルコキシシラン及びその部分加水分解縮合物、末端トリアルコキシシリル基封鎖のメチルヒドロジェンポリシロキサン、トリメトキシシリルプロピル変性環状メチルヒドロジェンポリシロキサン、トリアリルイソシアヌレート等を使用することができ、その配合量は、(A)成分100重量部に対して0~50重量部、好ましくは0.01~50重量部、より好ましくは0.01~10重量部程度とすることができる。

【0043】本発明組成物の硬化条件は用途において適宜選定することができるが、通常60~150℃で2~120分程度の範囲で行われる。

【0044】

【発明の効果】本発明のオルガノポリシロキサン組成物は、保存性と硬化性が両立したものである。

【0045】

【実施例】以下、触媒の合成例と実施例、比較例を挙げて本発明を具体的に説明するが、本発明は下記実施例に限定されるものではない。なお、下記例中の部は重量部を示す。

【0046】〔触媒合成例1〕白金原子として5,000ppmのシロキサン変性白金錯体のトルエン溶液中に、トルエンと同量の融点78℃の $C_6H_5SiO_{3/2}$ 単位及び $(CH_2=CH)SiO_{3/2}$ 単位を含有してなるフェニル基及びビニル基含有シリコンレジンを追加し、均一になるまで攪拌し、スプレードライ法によりレジnpowder白金触媒（触媒1、白金原子量：5,000ppm）を調製した。

【0047】〔触媒合成例2〕3,6-ジメチル-4-オクチン-3,6-ジオール（融点54℃）5gに、塩化白金酸から誘導されたビニル基含有シロキサン錯体5gを加え、80℃にて1時間熱処理し、ストリップした後、冷却して固体のヒドロシリル化触媒（触媒2、白金原子量：5,000ppm）を調製した。

【0048】〔触媒合成例3〕1,3-ビス（トリメチルシリルエチル）ベンゼン（融点58℃）5gに、塩化白金酸から誘導されたビニル基含有シロキサン錯体5gを加え、80℃にて1時間熱処理し、これにポリグリセリン系界面活性剤0.5gを追加し、水中で乳化処理した後、濾過、乾燥して微粉状のヒドロシリル化触媒（触媒3、白金原子量：5,000ppm）を調製した。

【0049】〔実施例1〕分子鎖両末端がビニルジメチルシリル基で封鎖された25℃の粘度が30,000cpのジメチルポリシロキサン100部と、表面がジクロロシランで処理された比表面積130m²/gの煙霧状シリカ10部を万能混合機に入れて均一になるまで混合を行い、ベースコンパウンドを調製した。

【0050】このベースコンパウンド100部に対して、上記触媒合成例1にて得た触媒1を2.0部（前記ベースコンパウンドに対して白金換算で100ppm）、触媒合成例1において使用したものと同様のシロキサン変性白金錯体のトルエン溶液を0.1部（前記ベースコンパウンドに対して白金換算で5.0ppm）、及び2-エチルヘキサノールを0.002部添加し、万能混合機にて均一になるまで攪拌した後、更に両末端がトリメチルシリル基で封鎖されたSiH基0.005mol/gを有するメチルヒドロジェンポリシロキサンを16部加えて混合し、組成物1（（D）成分中の白金原子に対する（E）成分中の白金原子の重量比は0.05%）を得た。

【0051】〔実施例2〕分子鎖両末端がビニルジメチルシリル基で封鎖された25℃の粘度が30,000cpのジメチルポリシロキサン100部と、表面がジクロロシランで処理された比表面積130m²/gの煙霧状シリカ10部を万能混合機に入れて均一になるまで混合

を行い、ベースコンパウンドを調製した。

【0052】このベースコンパウンド100部に対して、水を0.2部、触媒1を1.0部（ベースコンパウンドに対して白金換算で50ppm）、触媒合成例1で使用したものと同様のシロキサン変性白金錯体のトルエン溶液を0.01部（ベースコンパウンドに対して白金換算で0.5ppm）、及び2-エチルヘキサノールを0.002部添加し、万能混合機にて均一になるまで攪拌した後、更に両末端がトリメチルシリル基で封鎖された25℃の粘度が40cpのメチルヒドロジェンポリシロキサン（SiH基量が0.016mol/g）を5部及びフェニルシランを0.3部加えて混合し、組成物2（（D）成分中の白金原子に対する（E）成分中の白金原子の重量比は0.01%）を得た。

【0053】〔実施例3〕分子鎖両末端がビニルジメチルシリル基で封鎖された25℃の粘度が30,000cpのジメチルポリシロキサン100部と、表面がジクロロシランで処理された比表面積130m²/gの煙霧状シリカ10部を万能混合機に入れて均一になるまで攪拌し、ベースコンパウンドを調製した。

【0054】このベースコンパウンド100部に対して、水を0.2部、触媒2を1.0部（ベースコンパウンドに対して白金換算で50ppm）、触媒合成例1で使用したものと同様のシロキサン変性白金錯体のトルエン溶液を0.01部（ベースコンパウンドに対して白金換算で0.5ppm）、及び2-エチルヘキサノールを0.002部添加し、万能混合機にて均一になるまで攪拌した後、更に両末端がトリメチルシリル基で封鎖された25℃の粘度が40cpのメチルヒドロジェンポリシロキサン（SiH基量が0.016mol/g）を5部及びフェニルシランを0.3部加えて混合し、組成物3（（D）成分中の白金原子に対する（E）成分中の白金原子の重量比は0.01%）を得た。

【0055】〔比較例1〕分子鎖両末端がビニルジメチルシリル基で封鎖された25℃の粘度が30,000cpのジメチルポリシロキサン100部と、表面がジクロロシランで処理された比表面積130m²/gの煙霧状シリカ10部を万能混合機に入れて均一になるまで攪拌し、ベースコンパウンドを調製した。

【0056】このベースコンパウンド100部に対して、触媒1を2.1部（ベースコンパウンドに対して白金換算で105ppm）添加し、万能混合機にて均一になるまで攪拌した後、更に両末端がトリメチルシリル基で封鎖されたSiH基0.005mol/gを有するメチルヒドロジェンポリシロキサンを16部加えて混合し、組成物4を得た。

【0057】〔比較例2〕分子鎖両末端がビニルジメチルシリル基で封鎖された25℃の粘度が30,000cpのジメチルポリシロキサン100部と、表面がジクロロシランで処理された比表面積130m²/gの煙霧状

シリカ10部を万能混合機に入れて均一になるまで攪拌し、ベースコンパウンドを調製した。

【0058】このベースコンパウンド100部に対して、触媒合成例1で使用したものと同様のシロキサン変性白金錯体のトルエン溶液を2.1部（ベースコンパウンドに対して白金換算で105ppm）、及び2-エチルヘキサノールを0.002部添加し、万能混合機にて均一になるまで攪拌した後、更に両末端がトリメチルシリル基で封鎖されたSiH基0.005mol/gを有するメチルハイドロジェンポリシロキサンを16部加えて混合し、組成物5を得た。

【0059】〔比較例3〕分子鎖両末端がビニルジメチルシリル基で封鎖された25℃の粘度が30,000cpのジメチルポリシロキサン100部と、表面がジクロロシランで処理された比表面積130m²/gの煙霧状シリカ10部を万能混合機に入れて均一になるまで攪拌し、ベースコンパウンドを調製した。

【0060】このベースコンパウンド100部に対して、触媒1を2.1部（ベースコンパウンドに対して白金換算で105ppm）、及び2-エチルヘキサノールを0.002部添加し、万能混合機にて均一になるまで攪拌した後、更に両末端がトリメチルシリル基で封鎖されたSiH基0.005mol/gを有するメチルハイドロジェンポリシロキサンを16部加えて混合し、組成物6を得た。

【0061】〔比較例4〕分子鎖両末端がビニルジメチルシリル基で封鎖された25℃の粘度が30,000cpのジメチルポリシロキサン100部と、表面がジクロロシランで処理された比表面積130m²/gの煙霧状シリカ10部を万能混合機に入れて均一になるまで攪拌し、ベースコンパウンドを調製した。

【0062】このベースコンパウンド100部に対して、水を0.2部、触媒2を1.01部（ベースコンパ

ウンドに対して白金換算で50.5ppm）、及び2-エチルヘキサノールを0.002部添加し、万能混合機にて均一になるまで攪拌した後、更に両末端がトリメチルシリル基で封鎖された25℃の粘度が40cpのメチルハイドロジェンポリシロキサン（SiH基量が0.016mol/g）を5部及びフェニルシランを0.3部加えて混合し、組成物7を得た。

【0063】〔実施例4〕分子鎖両末端が水酸基で封鎖された25℃の粘度が20,000cpのジメチルポリシロキサン100部と、表面がジクロロシランで処理された比表面積130m²/gの煙霧状シリカ10部を万能混合機に入れて均一になるまで攪拌し、ベースコンパウンドを調製した。

【0064】このベースコンパウンド100部に対して、水を0.2部、触媒3を1.0部（ベースコンパウンドに対して白金換算で50ppm）、触媒合成例1で使用したものと同様のシロキサン変性白金錯体のトルエン溶液を0.01部（ベースコンパウンドに対して白金換算で0.5ppm）、及び2-エチルヘキサノールを0.002部添加し、万能混合機にて均一になるまで攪拌した後、更に両末端がトリメチルシリル基で封鎖された25℃の粘度が40cpのメチルハイドロジェンポリシロキサン（SiH基量が0.016mol/g）を5部加えて混合し、組成物8（（D）成分中の白金原子に対する（E）成分中の白金原子の重量比は0.01%）を得た。

【0065】得られた組成物1～8について、以下の実験を行った。まず、実施例1、比較例1、2、3については、キュラストメーターにて硬化性の差を確認した。測定の結果を表1に示す。

【0066】

【表1】

		10%トルク時間 (min)	90%トルク時間 (min)	90%トルク時間－ 10%トルク時間 (min)
実施例	1	5.0	6.5	1.5
	2	4.2	7.5	3.3
比較例	1	0.8	1.6	0.8
	2	6.0	10.5	4.5

【0067】表1に示すように、比較例1の通常のマイクロカプセル化白金触媒（即ち、（D）成分のみ）では硬化の立ち上がりから硬化の終了までの時間が3分以上かかっている。また、比較例2の無処理の白金触媒（即ち、（E）成分）に少量の制御剤を添加した系では、硬化の立ち上がりまでの時間が短い分、室温での十分な可使用時間は得られず、室温で保存した場合、3時間でゲル化してしまった。比較例3のマイクロカプセル化白金触

媒（（D）成分）に制御剤を加えた系では、比較例1よりも10%トルク時間が長くはなるが、10%トルク時間から90%トルク時間までの時間が極めて長く、硬化終了までに時間がかかりすぎる。これに対して実施例1では、比較例1よりもポットライフが長くなると共に、硬化終了までの時間は短くなり、長いポットライフと速やかな硬化特性が得られていることがわかる。この場合、マイクロカプセル化白金触媒（（D）成分）の濃

度、後で加える制御剤（（F）成分）の添加量、白金触媒（（E）成分）の添加量によって、望むポットライフと硬化スピードを併せ持つ組成物を得ることができる。

【0068】次に、実施例2、3、4及び比較例4については、120℃、20分の硬化条件にてスポンジ状の

発泡体に硬化発泡させた後のセル状態にて比較した。結果を表2に示す。

【0069】

【表2】

	実施例2	実施例3	比較例4	実施例4
硬化前状態	微小発泡あり	微小発泡あり	発泡なし	微小発泡あり
硬化後のセル状態	1mm以下 (セルは微小で 均一であった)	1mm以下 (セルは微小で 均一であった)	2mm以上 (セルは大きく かつ不均一であ った)	1mm以下 (セルは微小で 均一であった)

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